U.S. DEPARTMENT OF COMMERCE
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PB-277 463

International Conference on Oxidants, 1976 Analysis of Evidence and Viewpoints. Part VI The Issue of Air Quality Simulation Model Utility

California Inst. of Technology, Pasadena

Prepared for

Environmental Sciences Research Laboratory, Research Triangle Park, N.C.

Nov 77

EPA-600/3-77-118
November 1977

PB 277 463

Ecological Research Series

INTERNATIONAL CONFERENCE ON OXIDANTS, 1976 - ANALYSIS OF EVIDENCE AND VIEWPOINTS

Part VI. The Issue of Air Quality Simulation Model Utility

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/3-77-118		PB277463

4. TITLE AND SUBTITLE

INTERNATIONAL CONFERENCE ON OXIDANTS, 1976 - ANALYSIS OF EVIDENCE AND VIEWPOINTS
Part VI. The Issue of Air Quality Simulation Model Utility

5. REPORT DATE
November 1977

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
1. John H. Seinfeld
2. Kent R. Wilson

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
1. California Inst. of Technology, Pasadena, CA.
2. Univ. of California-San Diego, La Jolla, CA.

10. PROGRAM ELEMENT NO.
1AA603 AJ-13 (FY-76)

11. CONTRACT/GRANT NO.
1. DA-7-2143A
2. DA-7-2191J

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Sciences Research Laboratory - RTP, NC
Office of Research and Development
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE
EPA/600/09

15. SUPPLEMENTARY NOTES
Partially funded by the Office of Air Quality Planning and Standards.

16. ABSTRACT

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John H. Seinfeld, California Institute of Technology, and Kent R. Wilson, University of California at San Diego, review the issue of Air Quality Simulation Model (AQSM) utility. The strengths and weaknesses of the various modeling techniques are discussed, and the authors offer their recommendations on future studies.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air pollution * Computerized simulation * Utilization		13B 14B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	124
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	A06-A01

EPA Form 2220-1 (9-73)

EPA-600/3-77-118
November 1977

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Part VI. The Issue of Air Quality Simulation Model Utility

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ABSTRACT

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The more than one hundred presentations and discussions at the Conference revealed the existence of several issues and prompted the EPA to sponsor a followup review/analysis effort. The followup effort was designed to review carefully and impartially, to analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere), and to attempt to resolve some of the oxidant-related scientific issues. The review/analysis was conducted by experts (who did not work for the EPA or for industry) of widely recognized competence and experience in the area of photochemical pollution occurrence and control.

John H. Seinfeld, California Institute of Technology, and Kent R. Wilson, University of California at San Diego, review the issue of Air Quality Simulation Model (AQSM) utility. The strengths and weaknesses of the various modeling techniques are discussed, and the authors offer their recommendations on future studies.

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ACKNOWLEDGMENTS

These contracts were jointly funded by the Office of Research and Development (Environmental Sciences Research Laboratory) and the Office of Air Quality Planning and Standards.

The assistance of the technical editorial staff of Northrop Services, Inc. (under contract 68-02-2566) in preparing these reports is gratefully acknowledged.

INTRODUCTION

Basil Dimitriades and A. Paul Altshuller

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The one hundred or so presentations and discussions at the Conference revealed the existence of several issues and prompted EPA to sponsor a followup review/analysis effort. Specifically, this followup effort is to review carefully and impartially and analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere) and to attempt to resolve some of the oxidant-related scientific issues. This review/analysis effort has been contracted by EPA to scientists (who do not work for EPA or industry) with extensive experience and expertise in the area of photochemical pollution occurrence and control. The first part of the overall effort, performed by the EPA Project Officer and reported in a scientific journal (1), was an explanatory analysis of the problem and definition of key issues, as viewed within the research component of EPA. The reports of the contractor expert/reviewer groups offering either resolutions of those issues or recommendations for additional research needed to achieve such resolutions are presented in the volumes composing this series.

This report presents the reviews/analyses prepared by the contractor experts on the issue of air quality simulation model utility. In the interest of completeness the report will include also an introductory discussion of the issue, taken from Part I. The reviews/analyses prepared by the contractor experts follow.

THE ISSUE OF AIR QUALITY SIMULATION MODEL UTILITY

Basil Dimitriades and A. Paul Altshuller

Relationships between emissions and oxidant-related air quality are being pursued following three distinct approaches that differ mainly in degree of empiricism. In order of decreasing empiricism these approaches are:

1. *Empirical Approach.* The approach entails statistically or non-statistically associating ambient oxidant-related air quality data either with ambient concentrations of precursors or with precursor emissions rates. These asscciations clearly are not of cause-effect nature, and their intended use is not to predict absolute air quality; rather, it is to predict changes in air quality resulting from changes in emission rates.

2. *Smog Chamber Approach.* The approach entails deriving cause-effect relationships between oxidant and precursors through laboratory testing. This approach could be characterized as semiempirical because the relationships are derived from laboratory observations alone; they are not the product of theoretical derivations. Further, as in the preceding case, this approach is intended to predict only changes in air quality resulting from changes in emission rates.

3. *Mathematical Modeling (or AQSM) Approach.* The approach entails deriving the requisite air quality-emission relationships entirely from theory. Its intended use is to predict both absolute levels of and changes in air quality from given emission rate and meteorological data.

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To be usable, all methods of relating air quality to emissions, regardless of approach, must be validated and evaluated for accuracy. The distinction between "validation" and "accuracy-evaluation" follows. Validation refers to the agreement between model-predictions and observations when the input information fed into the model is perfectly accurate; thus, validation is the process of checking the validity of the principle underlying the method. Accuracy-evaluation refers to the agreement between model-predictions and observations for a model based on a perfectly sound principle; thus, accuracy-evaluation is an assessment of the error introduced by inaccuracies of the input information. Another term often used in connection with model evaluation is "verification," referring to the agreement between predictions and observations for the specific case in which the observations used for verification were taken from the same pool of data used to develop the model. This is the case, for example, of development and verification of AQSMs from the St. Louis RAPS data. In the discussion here, verification will be considered to be a limited form of validation.

Between validation and accuracy-evaluation, the latter appears to be relatively simpler, especially for the empirical and semiempirical methods and for the relatively simple AQSM methods. Thus, useful accuracy evaluations can be made from estimates of the errors associated with the input information and from numerical sensitivity tests to determine the impacts of such errors upon model-predictions. Unlike accuracy-evaluation, complete and direct validation of a model is extremely difficult — if at all possible — to accomplish for the main reason that the requisite "real world" data - on air quality and emissions — are either not available or not easy to obtain. Thus, for the empirical and semiempirical models relating emission changes to air quality changes, data on such changes either do not exist, or, if they do exist, as for the Los Angeles basin, they are useful only for verification of a "local-use" model. For the AQSM methods, intended to relate absolute levels of air quality to emissions rates, validation hinges upon solution of several problems, one of which is the definition of absolute air quality in terms of commonly obtained air quality monitoring data. *At the present time,* these problems in validating models are considered to be prohibitive by some inves-

tigators, but not insurmountable by others. *It is this latter disagreement among investigators that constitutes the issue to be examined here.*

More specifically, the question at issue here is:

- At the present time, are there any air quality simulation models sufficiently validated/evaluated and appropriate for use in designing urban oxidant control strategies?

The Environmental Protection Agency has not issued nor does it have plans for immediate issuance of strategy design guidelines (for oxidant control) involving use of AQSMs. Furthermore, EPA is conducting an extensive study (RAPS project) to first verify and subsequently further validate and evaluate several of the presently available AQSMs. Obviously, therefore, EPA does not feel that *at this time* there are AQSMs ready for use. Contrary to this EPA viewpoint, some investigators have suggested that there is one sufficiently validated air quality simulation model (Bell Lab). The Bell Lab Model was discussed at the International Conference; however, the more detailed description of the model and justification of the Bell Lab viewpoint are to be found in a subsequently published journal article (2).

There have been numerous reports, presented at the International Conference and elsewhere, on the principle, status of validation, and intended utility of several AQSMs. It is important, however, to make the distinction between true model applications and model exercises that merely demonstrate the *intended* utility of a model. The judgment called for here is on whether there can be true model applications, that is, on *whether there are models presently available which can and should be used immediately in designing urban oxidant control strategies.*

REVIEW AND ANALYSIS

John H. Seinfeld

INTRODUCTION

The purpose of this report is to address the question:

- At the present time are there any air quality simulation models* sufficiently validated/evaluated and appropriate for use in designing urban oxidant control strategies?

The following section is devoted to a brief summary of the basic mathematical relationships underlying air quality simulation models (hereafter denoted by AQSMs). The mathematical bases and assumptions inherent in all common AQSMs have been covered in detail elsewhere (3), and we choose not to reiterate that material here. We present only those concepts necessary to discuss the validity and accuracy-evaluation of AQSMs.

In the third section, we review the elements of several of the currently available AQSMs. We have chosen not to review all available AQSMs for photochemical oxidant. Only those AQSMs are reviewed that, in the author's opinion, are candidates for use by EPA in designing urban oxidant control strategies. The purpose of the review is to compare carefully the different manners of treatment of key physical and chemical processes in the principal AQSMs.

The fourth section is devoted to a discussion of the sources of uncertainty in AQSMs. In particular, we focus on those elements of AQSMs that have substantial

*As used here, air quality simulation model will be taken to represent a physicochemical model based on theoretical treatments of atmospheric chemistry and meteorology.

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bearing on oxidant prediction and for which there are elements of some uncertainty, arising either from lack of knowledge of the fundamental physics and chemistry or from inaccuracies in input information.

The fifth section contains an assessment of the accuracy of AQSMs. In this section we seek to answer the question posed at the outset.

In the sixth and final section, we provide conclusions and recommendations.

FUNDAMENTALS OF AQSMs

All conventional atmospheric diffusion models are based on the equation of conservation of mass:

$$\frac{\partial c_i}{\partial t} + u\frac{\partial c_i}{\partial x} + v\frac{\partial c_i}{\partial y} + w\frac{\partial c_i}{\partial z} = D_i\left(\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} + \frac{\partial^2 c_i}{\partial z^2}\right) + R_i(c_i,\ldots c_N,T) + S_i(x,y,z,t) \qquad \text{(Eq. 1)}$$

where c_i is the concentration of species i; u, v, and w are the fluid velocities in the three coordinate directions; D_i is the molecular diffusivity of species i in air; R_i is the rate of generation (or the negative of the rate of disappearance) of species i by chemical reactions at temperature T; and S_i is the rate of injection of species i into the fluid from sources.

Substituting the usual mean and fluctuating terms into Equation 1 and averaging the resulting equation over the ensemble of flows, we obtain the equation governing the ensemble average concentration $\bar{c}_i$. In atmospheric applications, the molecular diffusion term is negligible when compared to that representing advective transport. Thus, neglecting the contribution of molecular diffusion, the equation for $\bar{c}_i$ is

$$\frac{\partial \bar{c}_i}{\partial t} + \bar{u}\frac{\partial \bar{c}_i}{\partial x} + \bar{v}\frac{\partial \bar{c}_i}{\partial y} + \bar{w}\frac{\partial \bar{c}_i}{\partial z} + \frac{\partial}{\partial x}\overline{u'c_i'} + \frac{\partial}{\partial y}\overline{v'c_i'} + \frac{\partial}{\partial z}\overline{w'c_i'} = \overline{R_i(c_1,\ldots,c_N,T)} + \bar{S}_i(x,y,z,t) \qquad \text{(Eq. 2)}$$

Equation 2 is a rigorously valid equation for $\bar{c}_i$ (neglecting, of course, molecular diffusion); and, if the variables $\overline{u'c_i}$, $\overline{v'c_i}$, $\overline{w'c_i}$, and any of those arising from R_i are known as functions of space and time, it can be solved in principle to yield $\bar{c}_i$. Unfortunately $\overline{u'c_i}$ and so on cannot be measured at all points in an atmospheric flow and cannot be predicted exactly because of the closure problem of turblent flow. Thus, we must resort to models for these terms. The model employed in virtually all cases in which atmospheric flows are involved is that based on the concept of eddy diffusivities:

$$\overline{u'c_i'} = - K_H \frac{\partial \bar{c}_i}{\partial x} \qquad \overline{v'c_i'} = - K_H \frac{\partial \bar{c}_i}{\partial y} \qquad \overline{w'c_i'} = - K_V \frac{\partial \bar{c}_i}{\partial z} \qquad \text{(Eq. 3)}$$

The eddy diffusivities K_H and K_V are postulated to be functions of space and time (and not of $\bar{c}_i$ or any of its gradients).

Although there has been some study on the nature of terms of the form $\overline{c_i'^2}$ arising from turbulent chemical reactions, no atmospheric diffusion models for chemically reactive pollutants currently include expressions for these terms. All models neglect the contribution of turbulent concentration fluctuations to the mean reaction rate and employ the approximation,

$$\overline{R_i(c_1, \ldots, c_N, T)} \simeq R_i(\bar{c}_1, \ldots, \bar{c}_N, T) \qquad \text{(Eq. 4)}$$

The result of using Equations 3 and 4 in Equation 2 is the so-called atmospheric diffusion equation (ADE):

$$\frac{\partial \bar{c}_i}{\partial t} + \bar{u} \frac{\partial \bar{c}_i}{\partial x} + \bar{v} \frac{\partial \bar{c}_i}{\partial y} + \bar{w} \frac{\partial \bar{c}_i}{\partial z} = \frac{\partial}{\partial x}\left(K_H \frac{\partial \bar{c}_i}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_H \frac{\partial \bar{c}_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_V \frac{\partial \bar{c}_i}{\partial z}\right)$$

$$+ R_i(\bar{c}_1, \ldots, \bar{c}_N, T) + \bar{S}_i(x,y,z,t) \qquad \text{(Eq. 5)}$$

Because the governing equations are nonlinear, they must be solved numerically. Futhermore, the use of numerical techniques generally requires that the modeling region be subdivided into an array of grid cells, where each cell may have horizontal and vertical dimensions on the order of a few kilometers and several tens of meters, respectively. Before the general mass continuity equation can be solved, it must be "filtered" to remove all small scale variations that the grid cannot resolve, both in the concentration field and in the independent parameters, such as the wind velocities and the eddy diffusivities. The necessary filtering can be accomplished by averaging Equation 5 at each point over a volume equivalent to that of a grid cell. This spatial averaging will be denoted by the symbol < >. In addition, Equation 5 has been time-averaged over an interval equivalent to that used in each step of the numerical solution procedure. Thus, the concentration predictions obtained from Equation 5 represent spatially and temporally averaged quantities.

As a result of spatial averaging of Equation 5 we obtain*

$$\frac{\partial \langle \bar{c}_i \rangle}{\partial t} + \bar{u} \frac{\partial \langle \bar{c}_i \rangle}{\partial x} + \bar{v} \frac{\partial \langle \bar{c}_i \rangle}{\partial y} + \bar{w} \frac{\partial \langle \bar{c}_i \rangle}{\partial z} = \frac{\partial}{\partial x} \left(K_H \frac{\partial \langle \bar{c}_i \rangle}{\partial x} \right)$$

$$+ \frac{\partial}{\partial y} \left(K_H \frac{\partial \langle \bar{c}_i \rangle}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_V \frac{\partial \langle \bar{c}_i \rangle}{\partial z} \right) + \langle R_i (\bar{c}_i, \ldots, \bar{c}_N, T) \rangle + \langle \bar{S}_i \rangle$$

(Eq. 6)

As in the case of Equation 4, all models employ the approximation,

$$\langle R_i (\bar{c}_i, \ldots, \bar{c}_N, T) \rangle \approx R_i (\langle \bar{c}_i \rangle, \ldots, \langle \bar{c}_N \rangle, T)$$

(Eq. 7)

thereby neglecting the contribution of subgrid-scale concentration variations to the mean reaction rate.

---

*We assume that $\bar{u}$, $\bar{v}$, and $\bar{w}$ represent spatially averaged quantities by virtue of the manner in which they are determined.

Employing Equation 7 we obtain the equation that is the basis of all AQSMs,

$$\frac{\partial \langle \bar{c}_i \rangle}{\partial t} + \bar{u}\frac{\partial \langle \bar{c}_i \rangle}{\partial x} + \bar{v}\frac{\partial \langle \bar{c}_i \rangle}{\partial y} + \bar{w}\frac{\partial \langle \bar{c}_i \rangle}{\partial z} = \frac{\partial}{\partial x}\left(K_H \frac{\partial \langle \bar{c}_i \rangle}{\partial x}\right)$$

$$+ \frac{\partial}{\partial y}\left(K_H \frac{\partial \langle \bar{c}_i \rangle}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_V \frac{\partial \langle \bar{c}_i \rangle}{\partial z}\right) + R_i(\langle \bar{c}_1 \rangle, \ldots, \langle \bar{c}_N \rangle, T) + \langle \bar{S}_i \rangle \qquad \text{(Eq. 8)}$$

The *validity* of the atmospheric diffusion equation relates to how closely the predicted mean concentration $\langle \bar{c}_i \rangle$ corresponds to the true ensemble mean concentration. If the mean velocities, $\bar{u}$, $\bar{v}$, and $\bar{w}$, and the source emission rate S_i are known precisely at all points as a function of time, then, for an inert species, the only source of a discrepancy between the predicted and true mean concentrations is the eddy diffusivity model for the turbulent fluxes. If the true ensemble mean velocities and concentrations are known for an atmospheric flow, then it is relatively straightforward to assess the validity of Equation 8 for specified forms of K_H and K_V. Unfortunately, for any atmospheric flow the ensemble mean velocities and concentrations can never be computed since the atmosphere presents only one realization of the flow at any time. (Of course, for a statistically stationary flow, ensemble averages can be replaced by time averages. The atmosphere is, however, seldom in a stationary condition for any appreciable period of time.) Because the true mean velocities and source emission rates that are required to solve Equation 8 and the true mean concentration with which the solution of Equation 8 is to be compared are not available in general, an unambiguous measure of the validity of Equation 8 for any particular flow cannot be obtained.

Accuracy-evaluation refers to the agreement between model predictions and observations for a model based on a perfectly sound principle; thus, accuracy-evaluation is an assessment of the error introduced by

inaccuracies of the input information.* Whereas an assessment of model validity is very difficult to obtain, accuracy-evaluations can be made from estimates of the errors associated with the input information and from numerical sensitivity tests to determine the impacts of such errors on model predictions. Unlike verification and accuracy-evaluation, direct determination of the validity of an AQSM is extremely difficult to accomplish because the requisite exact data on emissions, meteorological variables, and air quality are neither available nor easy to obtain. It is therefore necessary to rely on combinations of verification and accuracy-evaluation studies to judge the adequacy of an AQSM. By necessity, we adopt this approach here.

Table 1 summarizes the sources of invalidity and inaccuracy of Equation 8. The sources of invalidity cannot be directly assessed for the reasons just stated. The sources of inaccuracy, on the other hand, can be assessed through verification and accuracy-evaluation studies.

The inputs needed to solve the atmospheric diffusion equation together with possible sources of error in those inputs are given in Table 1. In each instance unless the actual value of the input is known, the level of error in that input can only be estimated. From the standpoint of the effect of errors on the predictions of the equation, joint consideration must be given to the level of uncertainty in each input parameter and the sensitivity of the predicted concentrations to the parameter. Uncertainty relates to the possible error in the parameter from its true value, and sensitivity refers to the effect that variation in that parameter has on the solution of the equation. A parameter may have a large uncertainty associated with it but have

*Another term often used in connection with model evaluation is "verification," referring to the agreement between predictions and observations for the specific case in which the observations used for verification were taken from the same pool of data used to develop the input information for the model. Verification contains elements, therefore, of both validation and accuracy-evaluation. Henceforth, verification studies will be referred to as *validation* studies in keeping with the prevailing usage.

TABLE 1. SOURCES OF INVALIDITY AND INACCURACY IN AQSMs

Source of error	Comment
Sources of Invalidity	
True form of the turbulent fluxes, $\overline{u'c_i'}$, $\overline{v'c_i'}$, $\overline{w'c_i'}$, is unknown	Higher order closure models will offer improvement over eddy diffusivities in representing these terms. Such closure methods lead to large computational requirements.
Turbulent fluctuating chemical reaction terms are neglected (e.g. Equation 4)	Closure models appropriate for turbulent chemistry can be developed but large computational requirements as above may arise.
Effect of concentration fluctuations from spatial averaging on chemical reaction rate is neglected (e.g. Equation 7)	Introduce "micro-scale model" in regions where strong point and line sources occur.
Sources of Inaccuracy	
Mean velocities $\bar{u}$, $\bar{v}$, $\bar{w}$ are not true ensemble means (usually $\bar{u}$, $\bar{v}$, and $\bar{w}$ are calculated from data at a finite number of locations).	There is no way to determine the true mean from the data; $\bar{u}$, $\bar{v}$, $\bar{w}$ can be calculated in principle from accuracy fluid mechanical turbulence model.
Uncertainties in the measurement of wind speed and direction.	
Inadequate or non-representative spatial measurements of wind speed and direction.	
Uncertainties associated with wind field analysis techniques.	
Source emission function S_i is inaccurate.	More detailed emission inventories needed to reduce this source of inaccuracy.
Inaccurate or no specification of source location.	
Uncertainties in emission factors.	

(continued)

TABLE 1. (continued)

Sources of Inaccuracy	
Source of error	Comment
Inaccurate or no temporal resolution of emission. Inadequate or no verification of emission methodologies.	
Chemical reaction mechanism does not accurately reflect those chemical processes occurring in in the atmosphere. Uncertainties in experimental determinations of specific reaction rate constants. Variations of rate constants with temperature either uncertain or unknown. Inadequacies in lumping due to the non-representativeness of lumped class reactions relative to specific species within the class, e.g., reaction rates, products, and stoichiometric coefficients. Inaccuracies in the mechanism due to insufficient verification studies.	Continued study of chemical processes needed to ensure that R_i is accurate. Elimination or quantification of smog-chamber related errors: Inadequate or no control and measurement of levels of H_2O in the chamber. Impurities in background chamber air. Inadequate or no measurements of the spectral distribution and intensity of the chamber irradiation system. Inaccurate or ambiquous analytical methods. Non-homogeneity due to inadequate stirring or poor chamber design. Adsorption and desorption of reactants and products on chamber walls. Chemical reactions occurring on chamber surfaces. Inadequate control and measurement of chamber temperature.
Boundary conditions inaccurately specified. Concentrations Inversion height	No remedy except for more extensive data.

little influence on the solution. In such a case, effort at reducing the uncertainty in the parameter value may be unwarranted. On the other hand, small uncertainties in a parameter to which the solution is quite sensitive may have a large impact on uncertainties in the predicted concentrations. Thus, both uncertainty and sensitivity must be considered when the accuracy of the atmospheric diffusion equation is evaluated.

Finally, we note that discrepancies between predicted and measured concentrations may arise not only because of inaccuracies in input variables but also because concentrations are measured at a point, whereas the AQSM predicts spatially averaged concentrations. Measurement errors may also, of course, contribute to discrepancies between model predictions and data.

Although the validity of the atmospheric diffusion equation cannot be established without question, it is generally accepted that the equation is essentially a valid description of atmospheric transport, mixing, and chemical reaction processes. The major source of invalidity is the eddy diffusivity representation of the turbulent fluxes. However, as long as the eddy diffusivity functions used have been determined empirically under similar conditions to those to which the equation is applied, the equation should be considered valid. The principal problem, therefore, lies with the question of accuracy, namely the effect of uncertain specification of input parameters on the predictions of the model. It is primarily this issue on which we will concentrate subsequently.

Therefore, we conclude that:

- The atmospheric diffusion equation is essentially a valid description of atmospheric transport, mixing, and chemical reaction processes. The principal problems associated with AQSM utility are related to the accuracy of the equation, namely the specification of input relationships and parameters.

CURRENTLY AVAILABLE AQSMs FOR PHOTOCHEMICAL OXIDANT

In this section we summarize the salient features of several AQSMs currently available. Since the question posed at the outset refers to AQSMs sufficiently validated/evaluated and appropriate for use in designing urban oxidant control strategies, we restricted our attention to AQSMs currently available.

Summary of Available AQSMs for Photochemical Oxidant

Table 2 contains a summary of the four AQSMs to be evaluated in this report. Each of the AQSMs in Table 2 can be viewed as evolving from Equation 8. The SAI model is based directly on Equation 8 with no further simplifying assumptions. The LIRAQ model is based on the equation obtained by integrating Equation 8 with respect to the vertical coordinate z from the ground to the base of an elevated inversion layer. (Prior to this integration, assumed vertical concentration profiles are used in Equation 8.) The DIFKIN model is that form of Equation 8 obtained when one transforms to a coordinate system moving with the mean ground-level wind velocity and neglects horizontal turbulent diffusion and wind velocity changes with height (4). The Bell Laboratories model is obtained by integrating Equation 8 over all three coordinate directions to produce one (or more) well-mixed cells.

Chemical Kinetics

There are essentially two approaches that have been followed in developing kinetic mechanisms for photochemical smog:

- Lumped mechanisms - Mechanisms in which organic species are grouped according to a common basis such as structure or reactivity. Examples include the mechanisms of Hecht and Seinfeld, Eschenroeder and Martinez, Hecht et al., MacCracken and Sauter, and Whitten and Hogo (5-9).

TABLE 2. CURRENTLY AVAILABLE AQSMs FOR PHOTOCHEMICAL OXIDANT

Group	Description of AQSM	Species	References
Systems Applications Inc. (SAI)	Three-dimensional grid model based on numerical solution of the atmospheric diffusion equation. Three-dimensional wind field derived from ground-level measurements. Pollutants emitted from ground-level sources are injected into the bottom layer of grid cells; emissions from stacks are distributed among the grid cells aloft. 36-step kinetic mechanisms derived from the Hecht/Seinfeld/Dodge (1974) mechanism. Numerical solution by method of fractional steps with advection treated by SHASTA algorithm (93), vertical diffusion and chemistry by Crank-Nicholson method.	NO, NO_2, O_3, HNO_2.	(20, 94, 95)
		H_2O_2, paraffins,	(96)
		olefins, aromatics, aldehydes, unreactive hydrocarbons, SO_2, CO	(67, 97, 98)
			(9)
Lawrence Livermore Laboratory (LIRAQ)	Predicts the temporal variation of pollutant concentrations in a two-dimensional array of grid cells. Each cell is bounded on the bottom and top by the terrain and inversion base, respectively. For computational purposes, the pollutants are assumed to be well-mixed in each cell. An empirical algorithm is used to relate the cell-averaged concentration to the predicted ground-level value. A two-dimensional wind field is used. Pollutants emitted at ground level and aloft are injected uniformly into the appropriate well-mixed cell. 48-step chemical reaction mechanism, similar in nature to the Hecht/Seinfeld/Dodge mechanism is used. The governing equations are solved using a modified version of Gear's method (99).	NO, NO_2, O_3, HCL	(8)
		(olefins and highly reactive aromatics), HC2 (paraffins less-reactive aromatics and some Oxygenates), HC4 (aldehydes, some aromatics and ketones), HNO_2, N_2O_5, H_2O_2, RO_2, HO_2,	
		RCO_2, RNO_2, CO.	

(continued)

TABLE 2. (continued)

Group	Description of AQSM	Species	References
Environmental Research and Technology (DIFKIN)	Trajectory model based on a moving column of air in which vertical diffusion and chemical reactions take place. Pollutants are emitted into the appropriate vertical cell. The column of air follows a surface trajectory interpolated from surface wind data. 12-step kinetic machanism. Governing equations are written in the form of ordinary differential equations and solved using a Pade' approximation method.	NO, NO_2, O_3, reactive hydrocarbons, unreactive hydrocarbons, CO.	(6) (101)
Bell Laboratories	Three well-mixed cells in series. Wind is represented by volumetric air flow from cell to cell. Emissions instantaneously mixed in cell. 143-step kinetic mechanism based on detailed chemistry of propylene, formaldehyde, acetaldehyde, and propionaldehyde[c]. (interaction between free radicals and aerosols included.) Governing ordinary differential equations solved by Gear's method (100).	76 species, including NO, NO_2, O_3, propylene, formaldehyde, acetaldehyde, propionaldehyde, SO_2.	(2)

[a]The 36-step mechanism included 5 reactions describing SO_2 oxidation.

[b]The 48-step LIRAQ mechanism does not include SO_2 oxidation.

[c]The 143-step mechanism includes 19 reactions describing SO_2 oxidation.

- Surrogate mechanisms - Mechanisms in which organic species in a particular class, e.g., olefins, are represented by a single member of that class, e.g., propylene. Examples include the mechanisms of Niki et al., Demerjian et al., Dodge, and Gradel et al., (2, 10-12).

Of the four AQSMs in Table 2, three employ lumped mechanisms and one employs a surrogate mechanism. In general, the surrogate mechanisms tend to be more lengthy than lumped mechanisms because within a surrogate mechanism each individual species is treated as a separate chemical entity. For this reason surrogate mechanisms have not found wide utility in AQSMs that have substantial meteorological treatments because of the computational requirements associated with calculating simultaneous chemistry and transport.

In this subsection we wish to compare the kinetic mechanisms in the SAI, Livermore, and Bell Laboratories models. We do not consider the mechanism in DIFKIN since it is merely a single hydrocarbon special case of the other two lumped mechanisms. Our object here is to ascertain if there are any substantial differences among the three kinetic mechanisms.

Table 3 presents a comparison of the original Hecht/Seinfeld/Dodge mechanism, that contained in LIRAQ, and that contained in the present version of the SAI model. In Table 3 we list all the reactions that were included in the three mechanisms. If a particular reaction is included in a mechanism, then the rate constant value used in the mechanism is entered corresponding to the reaction in the column corresponding to the mechanism. The issue of most interest here is which reactions are included in which mechanisms and not the particular rate constant value adopted. (The rate constant values in all mechanisms continually undergo revision as new measurements become available.)

From Table 3 it is clear that, aside from rate constant differences, the three mechanisms are very similar, even though the interpretation of the lumped organic species varies somewhat among the mechanisms. Differences in rate constants are the result of choices from among avail-

TABLE 3. COMPARISON OF LUMPED CHEMICAL KINETIC MECHANISMS FOR PHOTOCHEMICAL SMOG

Reaction	Rate Constants @25°C (ppm, min units) Hecht/Seinfeld/Dodge[a]	LIRAQ[b]	SAI[c]
$NO_2 + h\nu \rightarrow NO + O$	VAR	VAR	VAR
$O + O_2 + M \rightarrow O_3 + M$	2.0×10^{-5}	2.0×10^{-5}	2.0×10^{-5}
$O_3 + NO \rightarrow NO_2 + O_2$	20.8	23.6	25.2
$O + NO + M \rightarrow NO_2 + M$	.0035	.0034	--
$O + NO_2 \rightarrow NO + O_2$	13800	13400	13400
$O + NO_2 + M \rightarrow NO_3 + M$	.0022	.0039	--
$O_3 + NO_2 \rightarrow NO_3 + O_2$	.046	.047	.05
$NO_3 + NO \rightarrow 2NO_2$	15000	13000	13000
$NO_3 + NO_2 \rightarrow N_2O_5$	4500	5600	--
$N_2O_5 \rightarrow NO_2 + NO_3$	15	12	--
$N_2O_5 + H_2O + \rightarrow 2HNO_3$	10^{-5}	6.8×10^{-6}	--
$NO + HNO_3 \rightarrow HNO_2 + NO_2$	.00025	--	--
$HNO_2 + HNO_3 \rightarrow H_2O + 2NO_2$	0.2	--	--
$NO + NO_2 + H_2O \rightarrow 2HNO_2$	2.1×10^{-6}	--	2.2×10^{-9}
$NO_2 + NO_3 + H_2O \rightarrow 2HNO_3$	--	--	1.66×10^{-3}
$2HNO_2 \rightarrow NO + NO_2 + H_2O$	4.5	--	--
$HNO_2 + h\nu \rightarrow OH + NO$	VAR	VAR	VAR
$OH + NO_2 \rightarrow HNO_3$	15000	10000	9000
$OH + NO + M \rightarrow HNO_2 + M$	12000	10000	9000
$OH + CO \rightarrow CO_2 + HO_2$	250	210	206
$HO_2 + NO \rightarrow OH + NO_2$	700	290	2000
$HO_2 + NO_2 \rightarrow HNO_2 + O_2$	--	44	20

(continued)

TABLE 3. (continued)

Reaction	Rate Constants @25°C (ppm, min units) Hecht/Seinfeld/ Dodge[a]	LIRAQ[b]	SAI[c]
$OH + HNO_3 \rightarrow H_2O + NO_3$	--	19	--
$HO_2 + OH \rightarrow H_2O + O_2$	--	29000	--
$HCl + O \rightarrow RO_2 + \alpha RCO_3 + (1-\alpha)HO_2$	6800	4400	5300(α=1)
$HCl + O_3 \rightarrow RCO_3 + RO + HC4$	.016	.018 ($\rightarrow HO_2 + RO + HC_4$)	.01
$HCl + O_3 \rightarrow$ OZONIDE	--	--	.005
$HCl + OH \rightarrow ROO + HC4$	25000	23000	38000
$HCl + OH \rightarrow ROO + H_2O$	--	14000	--
$HC2 + O \rightarrow ROO + OH$	107	73	37
$HC2 + OH \rightarrow ROO + H_2O$	8000	2900	8000
$HC2 + O_3 \rightarrow HCO_3 + HCHO + OH$	--	--	.002
$HC2 + NO_3 \rightarrow$ PROD	--	--	50
$HC3 + O \rightarrow ROO + OH$	65	--	20
$HC3 + OH \rightarrow ROO + H_2O$	3800	--	1300
$HC4 + h\nu \rightarrow \beta ROO + (2-\beta)HO_2$	VAR	VAR	VAR
$HC_4 + OH \rightarrow \beta RCO_3 + (1-\beta)HO_2 + H_2O$	23000	14000	100000(β=1)
$HC_4 + OH \rightarrow CO + HO_2 + H_2O$	--	7300	--
$HC_4 + O \rightarrow OH + HO_2 + CO$	--	290	--
$HC_4 + HO_2 \rightarrow H_2O_2 + RCO_3$	--	.0048	--
$HC_4 + NO_3 \rightarrow HNO_3 + RCO_3$	--	.22	--
$HC_4 + NO_3 \rightarrow CO + HNO_3 + HO_2$	--	0.5	--
$HC_4 + RO_2 \rightarrow ROOH + RCO_3$	--	.004	--

(continued)

TABLE 3. (continued)

Reaction	Rate Constants @25°C (ppm, min Units) Hecht/Seinfeld/Dodge[a]	LIRAQ[b]	SAI[c]
$HC_4 + h\nu \rightarrow CO + H_2$	--	--	VAR
$ROO + NO \rightarrow RO + NO_2$	910	2700	2000
$RCO_3 + NO \rightarrow ROO + NO_2 + CO_2$	910	1300	2000(R=H)
$RCO_3 + NO_2 \rightarrow PAN$	100	43	150
$RO + O_2 \rightarrow HO_2 + HC4$	.024	.0036	--
$RO + NO_2 \rightarrow RONO_2$	490	74	--
$RO + NO \rightarrow RONO$	250	74	--
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	5300	8200	4000
$HO_2 + RO_2 \rightarrow RO + OH + O_2$	100	98	4000 ($\rightarrow HC_3OOH+O_2$)
$ROO + ROO \rightarrow 2RO + O_2$	100	98	--
$HCO_3 + HO_2 \rightarrow HC(O)OOH + O_2$	--	--	10000
$PAN \rightarrow RCO_3 + NO_2$	--	--	.02

[a] In the Hecht et al. mechanism HC1, HC2, HC3, and HC4, refer to olefins, alkanes, aromatics, and aldehydes, respectively α represents the fraction of the total olefins containing terminal double bonds, and β is the formaldehyde fraction of the total aldehydes.

[b] In the LIRAQ mechanism HC1 denotes olefins and highly reactive aromatics, HC2 - paraffins, less reactive aromatics and some oxygenates, HC4-aldehydes, some aromatics and ketones.

[c] In the SAI model, a 31-step mechanism, called the carbon-bond mechanism, has been developed as a variation of the Hecht/Seinfeld/Dodge mechanism (9). Because of the association of reactions and reactivities with carbon bonds, the range of reactions and the range of rate constants in a kinetic mechanism can be narrowed somewhat if each atom is treated according to its bond type. In this mechanism, hydrocarbons are divided into four groups: single-bonded carbon atoms, fast bouble bonds (i.e., relatively reactive double bonds), slow double bonds, and carbonyl bonds. Single—bonded carbon includes not only paraffin molecules, but also the single-bonded carbon atoms of olefins, aromatics, and aldehydes. Double bonds are treated as a pair of carbon atoms. An activated aromatic ring is considered as three double bonds in the present formulation of the mechanism, and because of a similarity in reactivities, aromatics are lumped with the slow (ethylene) double bonds rather than with the fast double bonds. In the mechanism HC1, HC2, HC3, and HC4 represent fast double bonds, slow double bonds, single-bonded carbon atoms, and carbonyl bonds, respectively.

able rate constant values and more recent determinations as well as the result of different lumping schemes. We conclude that:

- With respect to the representation of chemical detail, the reaction mechanisms in the current versions of the SAI and LIRAQ models are essentially equivalent. The mechanisms in DIFKIN can be viewed as a special case of those in the former models.

The next point to consider is the comparison of the Bell Laboratories mechanism with those in the SAI and LIRAQ models. As noted above, the Bell Laboratories mechanism is a detailed mechanism based on the chemistry of propylene and the three lowest aldehydes. For the purpose of this section, our interest is to ascertain if the Bell Laboratories mechanism contains any fundamental chemical details not present in the SAI and LIRAQ mechanisms. In the inorganic chemistry, the Bell mechanism includes $O(^1D)$ chemistry and free radical (primarily HO_2) scavenging by aerosols, not included in the other two mechanisms. (We discuss these two processes subsequently.) With respect to the organic chemistry, appropriate combination of free radical reactions in the Bell mechanism can be shown to lead to the SAI and LIRAQ mechanisms. We conclude that:

- With respect to fundamental chemical detail, the Bell Laboratories mechanism, while more explicit than the SAI and LIRAQ mechanisms, is equivalent in nature to the latter two mechanisms.

The Treatment of Meteorological Variables

Table 4 summarizes the treatment of meteorological variables in the four AQSMs under consideration. In Table 4 the methods of treating advection and turbulent diffusion are summarized separately.

Initial and Boundary Conditions

The initial condition for the atmospheric diffusion equation is the concentration field at the time corresponding to the beginning of the simulation, $\langle \bar{c}_i(x,y,z,0) \rangle$. Simulations are normally begun at night or

TABLE 4. THE TREATMENT OF METEOROLOGICAL VARIABLES IN AQSMs FOR PHOTOCHEMICAL OXIDANT

Model	Advection	Mixing Depth	Turbulent Diffusion
SAI	Model requires a three dimensional wind field. In the 1973 version hourly averaged surface measurements are interpolated to a fine mesh. The surface field together with the lower boundary condition, w=0, is used to derive the vertical velocities. The surface u, v components are assumed to apply at all levels, and so w can be calculated from an application of the finite difference form of the continuity equation. The current version of the model employs upper level wind measurements and objective analysis procedures to render the wind field mass consistent. In the 1973 version, the horizontal wind components were assumed to be invariant with height. Sensitivity studies reported by Reynolds et al. (97) indicate that inclusion of wind shear effects in the model can alter NO_2 and ozone predictions significantly. Consequently, the capabilities of the model were expanded to treat wind shear phenomena. Theoretical wind shear relationships derived by Lamb (66) using the predictions of a planetary boundary layer model developed by Deardorff (102) are employed.	The mixing depth field is developed using area-wide interpolation. Temperature profiles from radiosondes and acoustic sounder measurements are the basic inputs used to determine the depth of the mixed layer.	Vertical eddy diffusivity coefficients K_v have been derived through use of a methodology developed by Lamb et al. (66, 103,104). In this procedure, employing flow fields predicted by the model of Deardorff (102), particles are released from a point and followed as they are transported downwind. From the particle trajectories, it is possible to calculate the pollutant concentration field downwind of the release point. Given the concentration and mean flow fields, the diffusivity profile is obtained through use of optimal control theory techniques. Horizontal eddy diffusivity coefficient K_H specified is an input parameter.

(continued)

TABLE 4. (continued)

Model	Advection	Mixing Depth	Turbulent Diffusion
SAI (Cont)	These relationships are useful in instances when wind measurements aloft are not available. For situations in which wind measurements are available both at the surface and aloft, an objective technique for preparing appropriate three-dimensional wind inputs to the model has been developed (98).		
LIRAQ	An approximate two-dimensional wind field is constructed using a Gaussian weighting function to interpolate sparse, three-hour average wind measurements to grid cells. An iterative variational procedure is used to refine the interpolated values so as to render the field mass consistent. A feature of the technique is that it allows a parameterized treatment of flow through the inversion base and around topographic features.	Mixing depths over the region are inferred from sparse surface measurements of temperature, elevated profile data, topography and the temperature advection from prevailing flows. These data are used to construct an interpolated field. The mixing depth is an important input parameter for the mass consistent wind field calculation.	Spatial and temporal variations of K_H calculated based on similarity theory. Inputs are root-mean-square dispersion, grid cell size, energy dissipation rate, mixing depth and reference height wind velocities. Although LIRAQ is a two-dimensional vertically integrated model, a value of K_V is required to establish boundary conditions for the vertical concentration profile. K_V determined from a power-law profile for wind speed and the assumption that the friction velocity is 0.1 x the horizontal velocity at a height of 1 m.
DIFKIN	The advection patterns used to derive the trajectories are obtained by using weighted averages of wind stations surrounding a particular point. The	Mixing depth data are deduced from airborne temperature measurements and acoustic soundings. Inversion base heights are required	Effect of horizontal diffusion ignored. K_V profile shapes determined to be trapezoidal from ground to inversion base. The magnitude of the profile is given as a function

(continued)

TABLE 4. (continued)

Model	Advection	Mixing Depth	Turbulent Diffusion
DIFKIN (Cont)	trajectories are constructed in hourly upwind segments from the measurement stations. In most cases the three nearest stations are used in a simple inverse distance weighting for the stepwise upwind tracing of an air parcel movement.	only at points along the air parcel trajectory.	of wind speed. Stability and surface properties not included in specification of K_v.
BELL	A 'bulk' wind flow along the axis of the cells is assumed; no detailed vertical or horizontal resolution is employed in the model. Wind speed variations throughout the day are defined from the medians of seasonal observation. These data are smoothed to provide a continuous temporal wind variation.	The mixing depth is averaged over each cell and only three spatial values are required. These data were determined from lidar measurements of vertical aerosol extent in combination with mixing height data obtained from other sources.	Diffusion in a cell is instantaneous.

at sunrise, and the $\langle c_{i_o} \rangle$ field at that time is constructed from the station readings. A ground-level interpolation routine and assumptions regarding the vertical variation of the concentrations are required to generate the full $\langle \bar{c}_{i_o} \rangle$ field from the station data. Because only surface readings are generally available from which to construct a $\langle \bar{c}_{i_o} \rangle$ field, we expect the most uncertainty in the initial conditions aloft.

The boundary conditions for Equation 8 consist of the concentrations upwind of the region, the pollutant fluxes at the ground (the source emissions), and the flux condition at the upper vertical boundary of the region. Concentrations upwind of the modeling region can be estimated if monitoring stations exist at the upwind edge of the airshed. In such a case uncertainties in these concentrations will be low when a previous time is simulated. The major source of uncertainty in boundary conditions generally arises at the upper vertical boundary. First, the temperature structure, for example, the height of the base of an elevated inversion layer, is not known precisely. Second, the pollutant flux condition at the boundary is also not known precisely.

Thus, the major uncertainty in boundary conditions lies in specifying the upper vertical boundary conditions, both the location of the boundary and the species flux condition at the boundary.

For each of the four models in Table 2 it is necessary to specify the initial concentrations of all species. For the grid models (SAI and LIRAQ) boundary pollutant concentrations must be specified at each time increment for all grid cells that lie along an inflow boundary from the ground to the upper vertical boundary of the region. For a trajectory model (DIFKIN) only initial concentrations need to be specified. The usual approach is to initiate the trajectory in the vicinity of an air monitoring station and use the observed measurements as initial concentrations in the lowest cell. As in all cases where vertical variations are included, the initial vertical distribution of concentrations must be assumed.

Source Emission Inventory

Table 5 summarizes the source emission inventories required for the four AQSMs by spatial, temporal, and species resolution.

SOURCES OF UNCERTAINTY IN AQSMs

In the previous section we summarized the key elements of four AQSMs for photochemical oxidant. The object of that section was to delineate the different treatments of the major physical and chemical processes. Now we proceed to consider the principal sources of uncertainty in the specification of these processes. In the following section we will attempt to estimate the levels of accuracy of the predictions of the four models given the prevailing sources of uncertainty.

Chemical Kinetics

The assessment of the accuracy of chemical kinetic mechanisms for photochemical smog has received a considerable amount of attention (7, 9, 10-13). In this subsection we consider the two most important aspects of this assessment.

- What are the major sources of uncertainty in current mechanisms (i.e., those in the four AQSMs of Table 2)?

- In reported mechanism validation studies can we draw general conclusions about the performance of the current mechanisms when simulating laboratory smog chamber data?

The levels of detail of the chemical mechanisms vary significantly among the four AQSMs. Each of the four mechanisms has been shown to be capable of representing the general chemical features of the photochemical smog system. The 12-step mechanism in DIFKIN is, however, too simplified

TABLE 5. SOURCE INVENTORIES REQUIRED FOR AQSMs FOR PHOTOCHEMICAL OXIDANT

Model	Spatial Resolution	Temporal Resolution	Species Resolution
SAI	Emissions are aggregated onto a 2x2 mile grid system. Large elevated source emissions are treated with a highly simplified plume model.	Requires temporally resolved data sufficient to represent the changes in emission levels. Hourly values are required for most pollutants with finer resolution, ~15 minutes, for emission sources that have a pronounced diurnal variation, e.g. power plants and mobile sources.	15-Step Mechanism. (1973 version) The basic emission input to the model from stationary and mobile sources are CO, RHC, UHC and NO_x. The fraction of NO_x emitted as NO_2, for each source class, must be specified by the user. UHC represents all unreactive hydrocarbons including C_1-C_3 paraffins, acetylene and benzene. In the model calculation all other hydrocarbons, RHC, in the atmosphere are considered to be reactive. 31-Step Mechanism The primary emissions are the same as the 15-step case with the RHC split into 4 basic classes: aromatics, olefins, aldehydes and alkanes.
LIRAQ	The LIRAQ model has been employed with a range of grid cell sizes from 1-5 km. For photochemistry the modeling region is restricted to approximately 400 cells. Pollutants emitted at ground level and aloft are injected uniformly into the appropriate well mixed cells. LIRAQ employs many data generation programs and as a consequence the grid resolution of the emission inventories can be readily varied.	Similar requirements to the SAI model.	Primary emissions for mobile and stationary sources are required for CO, NO_x, H_2O and three basic classes of hydrocarbons (essentially alkenes, alkanes, aldehydes).

(continued)

TABLE 5. (continued)

Model	Spatial Resolution	Temporal Resolution	Species Resolution
DIFKIN	The only spatial resolution required for a trajectory model is an area equivalent to the area of the column being advected. If a small number of trajectories are being considered, the data requirements can be quite minimal. Large numbers of trajectories can require spatial resolution of the same type used in the above models. Emission from elevated point sources are treated as volume sources.	The temporal resolution required of the emission data is simply that the emission level be prescribed as the column of air passes over a spatial point. The implied resolution at a point is then a function of local wind velocity. Temporal requirements are similar to the above models.	For the 12-step mechanism the emission inventory requirements are minimal: CO, NO and a simple split of the hydrocarbons. Low reactivity hydrocarbons include methane, ethane, propane, acetylene, methylacetylene, and benzene; all others are considered to be reactive.
BELL	Morris, Essex, and Hudson Counties, New Jersey, in the present version. Generally as three contiguous cells for future applications. Emissions are assumed to be fully and uniformly mixed within each cell below the mixing height.	Continuous variation of emissions with time corresponding to the integration time step of the model.	Sources divided as fixed and mobile. Mobile source emissions are NO, CO, SO_2, CH_4, CH_3CH_3, HCHO, CH_3CHO and reactive and inert hydrocarbons, represented as propylene and acetylene, benzene and propane, respectively. Stationary source emissions are NO, CO, SO_2, CH_4, CH_3CH_3, HCHO, CH_3CHO, and total hydrocarbons.

for detailed quantitative predictions. The 143-step mechanism in the Bell Laboratories model is more detailed than necessary, even if meteorological variations can be represented as simply as a few cells in series. Thus, the lumped mechanisms in the SAI and LIRAQ models represent a reasonable compromise between chemical detail and computational simplicity. Moreover, these mechanisms appear to represent properly the known chemical features of the system.

The most important inorganic reactions are common to the mechanisms in the SAI, LIRAQ, and Bell Laboratories models. There is some variability in the choice of which secondary inorganic reactions are included.* As noted in the previous section on the chemical kinetics of currently available AQSMs, the representation of organic reactions in the mechanisms is essentially similar (see Table 3).

With respect to sources of uncertainty in kinetic mechanisms, it is necessary to consider the performance of mechanisms in the simulation of smog chamber data. The best characterized data available appear to be those obtained at the University of California, Riverside (UCR). Of the mechanisms in the AQSM, the most detailed set of validation studies available are those for the SAI mechanism and the UCR data (9). Because of the essential similarity of the SAI and LIRAQ mechanisms, it is reasonable to discuss uncertainties in the predictions of both mechanisms based on the performance of the SAI mechanism.

The overall smog formation process as simulated by present mechanisms can be described in terms of two radical pools. One of these pools is

*In studies with the Bell Laboratories mechanism (see the following section), it was found that the removal of $O(^1D)$ chemistry had a noticeable effect on the predictions of the mechanism. Also, not included in these lumped mechanisms is radical scavenging by particles, an aspect included in the Bell Laboratories mechanism. In sensitivity studies, it was found that the removal of the radical scavenging term did not lead to substantially different predictions. Nevertheless, it would seem advisable that radical removal (principally HO_2) be included in the lumped mechanisms together with $O(^1D)$ chemistry.

the oxygen radical pool; it is associated with NO_2 photolysis and the production of ozone. The other radical pool can be referred to as the peroxy-oxyl radical pool. In this pool, radical transfer reactions convert peroxy radicals to oxyl radicals and vice versa, with the concomitant conversion of NO to NO_2 and oxidation of hydrocarbons. Oxyl radicals are formed when peroxy radicals convert NO to NO_2. Peroxy radicals are formed when hydroxyl radicals react with hydrocarbons, and hydroperoxy radicals are formed when alkoxyl radicals react with molecular oxygen.

A major problem with kinetic mechanisms for photochemical smog is that it is difficult to reproduce the initial rate of hydrocarbon disappearance and the initial rate of conversion of NO to NO_2. This difficulty is often resolved by adding some initial source of peroxy or oxyl radicals in addition to those formed by the reactions of oxygen atoms with hydrocarbons, for example, by assuming an initial concentration of nitrous acid, which photolyzes and supplies the initial radicals. Whether nitrous acid is initially present in the smog chambers in the amounts assumed is unknown.*

Once the pool of peroxy-oxyl radicals is established in a simulation, the radical pool must be maintained, because radical sinks, such as the reaction of hydroxyl radicals with NO_2 or peroxy-peroxy combination reactions, tend to consume more radicals than are produced by NO_2 photolysis and the subsequent reactions of oxygen atoms. The radical concentration is maintained in the mechanism by the photolysis of carbonyl compounds (and, in olefin systems by the ozone-olefin reactions). In some cases it is obvious that too many radicals are present initially and that the maintenance source of radicals in the mechanism is in-

*There is evidence that nitrous acid is found during the loading of smog chambers (14). The amount required to simulate UCR experiments was found by Whitten and Hogo (9) to be generally about one-third of the equilibrium concentration of nitrous acid that could form from the initial concentrations of NO, NO_2 and H_2O. Whether the walls of the smog chamber are an important source of initial radicals is unknown.

adequate. It has been speculated that the walls of the chamber in some way supply radicals to the peroxy-oxyl radical pool. The effect of such a process would be greatest when the concentration of normal radicals was the lowest — in a low activity and low hydrocarbon experiment. That the walls may be supplying radicals is supported by the similar need for a high initial HNO_2 concentration (relative to equilibrium). A second problem, noticeable in most of the SAI simulations of the UCR data, is the poor fit between predicted and measured NO_x concentrations. This problem is usually reflected by an overprediction of the NO_2 concentration, although it could also be caused by NO_x losses in the smog chamber.

In studies with the SAI mechanism and UCR butane photooxidation data, it was found that for many cases one could achieve a reasonable fit of predictions to measurements by using initial and maintenance sources of radicals within the bounds of uncertainty of the various reaction rates. However, it was not possible to obtain a good fit to measurements of systems in which the hydrocarbon/NO_x ratio and the rate of hydrocarbon oxidation are low. In simulating a series of experiments on the propylene/butane system, it was found that it was necessary to lower the carbonyl photolysis constant for radical production below that which had been established in earlier simulations. In toluene simulations in which the hydrocarbon/NO_x ratio was low, the inadequate maintenance radical problem arose. On the other hand, high hydrocarbon/NO_x experiments led to difficulties because of overly rapid radical production. In general, the mechanism does not provide enough maintenance radicals to sustain the rate of chemical reactivity observed at UCR. In general, the compound most poorly simulated is PAN. PAN concentrations can be simulated in runs with high concentrations of NO_x and propylene. For the low NO_x runs, however, the predicted PAN concentrations vary from too low to too high as the hydrocarbon concentration increases.

In a similar study, Dodge simulated "dirty" chamber effects by assuming the walls to be a source of propylene at a rate sufficient to explain the ozone yield obtained in a chamber experiment containing only background levels of hydrocarbon and NO_x (12).

The following aspects of kinetic mechanisms have been treated as "fitting" parameters wherein adjustments are made within accepted uncertainty limits to obtain as close a match as possible between predicted and measured concentrations (see the Appendix for a detailed discussion):

- Initial concentration of nitrous acid;
- Quantum yield of carbonyl photolysis;
- PAN chemistry;
- NO_x loss chemistry;
- Ozonide reactions;
- Chamber effects, such as desorption of hydrocarbons and free radicals from chamber walls.*

As discussed above, variation of these parameters is usually required to simulate the initiation and maintenance of the radical pool. An analysis of several of these factors and of their role in predictions is presented in the Appendix.

From the reported validation studies with kinetic mechanisms and smog chamber data a degree of uncertainty in absolute levels of ozone predictions of approximately ±50% is evident. Whether the source of discrepancy between mechanism predictions and smog chamber data is our lack of complete understanding of the prevailing chemistry or smog chamber effects cannot be established with certainty. The production of ozone in "clean" smog chambers is an indication that so-called chamber effects do exist, and areas of uncertainty as to mechanism and rate constants are clearly evident.

With respect to the sources of uncertainty in chemical kinetics we offer the following conclusions:

*In atmospheric applications any reaction steps required to represent chamber effects are removed from the mechanism.

- Although most mechanisms can represent the qualitative features of the photochemical smog system, there are still important sources of uncertainty in precise mechanisms, certain rate constants, and appropriate initial conditions.

- *Absolute* levels of ozone concentrations predicted by kinetic mechanisms probably have an associated uncertainty of ±50%. *Relative* changes in predicted ozone concentration levels resulting from changes in initial conditions probably have a somewhat lower uncertainty.

Meteorology

There are three basic meteorological variables of interest: the wind field, mixing depth, and solar insolation. A problem, common to all models, is that sparse and often unrepresentative measurements are used to derive continuous fields over the region. The key question is: how representative are the interpolated fields of the actual physical processes in the atmosphere? Roth et al. (15) in their study of wind measuring stations in the Los Angeles region found a substantial proportion of the data, taken at identical or adjacent sites at the same time, differed markedly. A 20% error in any of the measurements is not uncommon, the uncertainty in the vertical velocity field being somewhat greater. The basic effect of small perturbations in the wind field is to introduce an artificial diffusion or smoothing process. Larger errors can affect the time phasing and magnitudes of pollutant peaks at particular locations. Mass-consistent wind fields, derived using objective analysis procedures and appropriate weighting of station data, can substantially reduce the effects of uncertainties. The artificial creation of convergence and divergence zones can be minimized. Some problems still remain, however, in creating three-dimensional wind fields from very limited amounts of upper level data. To some extent errors in these measurements can often mask physically meaningful calculations of vertical velocities.

All models considered in this study require specification of the mixing depth. In most regions it is only measured, or calculated from temperature profiles, at a very limited number of locations. A 20-30%

error is typical; however, in regions of convergence or strong heating on surface slopes the accuracy can be much worse. (In view of the fact that concentration predictions are very sensitive to mixing depth, it is vital to use objective analysis procedures that simulataneously couple the calculation of the wind field and inversion base location.)

One of the most influential parameters in determining the ground level oxidant concentrations is the magnitude of the ultraviolet radiation intensity. Photodissociation rates are typically derived from measurements of total solar flux. This introduces an uncertainty in photolysis rates of approximately 20% because the reaction rates depend only on the UV portion of the solar spectrum. Broad band measurements are difficult to correct for cloud cover and aerosol loading effects. Extensive calculations were performed in the LIRAQ study in an attempt to circumvent this problem.

Initial and Boundary Conditions

Most models depend on routine air monitoring data for their initial and boundary conditions (I.C. and B.C.). These data are typically interpolated to a fine mesh to provide the surface level I.C. and the B.C. for the edges of the region. There are obvious problems with this approach:

(a) The monitoring data are often not representative of the concentration levels surrounding a monitoring station (see, for example, Ott and Eliassen (16)). The nature of this problem is site specific and must be evaluated for each monitoring site within the modeling region.

(b) The monitoring data represent surface level measurements. I.C. profile data are required for SAI and DIFKIN; all models require the concentration levels above the inversion base as an upper level B.C. This problem with B.C. can to a certain extent be eliminated by extending the vertical coordinate of the model domain above the inversion so background levels can be used. If this is not feasible, and depending on the atmospheric condition, a factor of three should be considered as the minimal level of uncertainty associated with upper level

boundary conditions. These uncertainty levels can be reduced if upper level measurements are available. The problem with upper level I.C.s can to a certain extent be eliminated by starting the model well before the time period of interest.

(c) The most serious problem associated with I.C. and B.C. may be uncertainties associated with the monitoring methods themselves. Trijonis (personal communication) has performed a critical review and statistical analysis of the quality of monitoring methods. Based on this work, the precision of the data corrected for interference effects is recommended to be: O_x/O_3 - excellent, NO_x - good (error 10%), total hydrocarbons - fair, and nonmethane hydrocarbons - poor. Of these data the largest uncertainty is in the nonmethane hydrocarbon data, which must be further split for validation according to the requirements of the particular chemical mechanism. A minimum of 50% uncertainty should be associated with these measurements unless more refined results are available.

Summarizing, for most models the major uncertainties are associated with the upper level data (factor of 3) and with the hydrocarbon measurement (~50%). The problem with horizontal boundary conditions can largely be removed by choosing the model boundaries away from strong gradients and pollutant sources. Initial conditions uncertainties can be minimized by starting the calculation well before the time period of interest.

Emission Inventories

The assessment of the level of uncertainty in a particular emission inventory is obviously a substantial undertaking and, most properly, should be carried out when the inventory itself is compiled.*

Emissions from each class of source can be characterized according to:

*Typical levels of uncertainties in mobile and fixed source activities (e.g., number of vehicle miles traveled and number of units of fuel consumed) should be identified. Then, the typical uncertainties in emission factors (e.g., grams per mile of pollutant emitted per vehicle mile traveled and gram of pollutant per unit of fuel consumed) should be combined with the uncertainties in activities to produce net uncertainties in emissions.

- Level of spatial resolution,
- Level of temporal resolution, and
- Source activity or emission factor.

The level of spatial resolution achievable is in principle as fine as one desires since the locations of all sources can presumably be specified (although traffic count data may not be available on a street-by-street basis). Temporal emission rates will fluctuate some from day to day. Emissions from some stationary sources may vary with ambient temperature, but these variations are generally known as a function of temperature. The major problem in properly specifying source emissions is uncertainty in emission quantities arising from uncertainties in source activities and emission factors.

Two basic factors are involved in emission specification, the quantity emitted and its composition. Emission compositions are typically estimated from handbooks such as AP-42. Each table in AP-42 includes a qualitative estimate of the accuracy of the material on a scale that varies from A (excellent) to E (poor). Recent studies aimed at establishing NO_x and SO_2 emission inventories for stationary sources in the South Coast Air Basin have presented estimates of the level of accuracy of the overall inventories (17). These reports estimate that a ±20% uncertainty in the total emissions is reasonable, whereas uncertainties in individual source emissions can range as high as ±300%. A compensating factor is that generally the large uncertainties are associated with small absolute emission levels. Mobile source emission estimates depend to a large extent on the quality of the traffic data. The level of uncertainty in the South Coast Air Basin mobile source emissions of NO_x, CO, and SO_2 is probably of the order of ±15%.

Probably the most serious emission inventory problems are those associated with hydrocarbon emissions. The level of uncertainty in the stationary source hydrocarbon emissions in the South Coast Air Basin is probably on the order of ±30%. Within individual source classes the

uncertainties can be as high as ±100%. Mobile source hydrocarbon emission uncertainties have been estimated in the range 15-50%. Two of the AQSMs under consideration, namely the SAI model and LIRAQ, require reactive hydrocarbon speciation in the emission inventory. (In the Bell Laboratories model all reactive hydrocarbons are represented as propylene.) Generally insufficient information is available concerning the hydrocarbon composition of major hydrocarbon sources. It is necessary to estimate a hydrocarbon breakdown into the four classes. (Aldehydes constitute an important class of reacting species, and virtually nothing is known about aldehyde emissions.) It is difficult to estimate the uncertainty associated with estimated hydrocarbon speciation. From the point of view of the AQSM, errors in absolute hydrocarbon levels will be more influential on oxidant predictions than will errors in class assignments because reactivities do not vary enormously for the classes. Thus, uncertainties in hydrocarbon emissions by class, while definitely leading to uncertainties in oxidant predictions, are not detrimental to accurate oxidant predictions as are uncertainties in hydrocarbon emissions by total level.

If we attempt to place overall uncertainty limits on the emissions for a region such as the South Coast Air Basin that has received considerable inventory attention, we might suggest the following ranges:

CO	±20%
NO_x	±20%
HC	±30%

These ranges represent limits for accuracy-evaluation studies.

Any technique for evaluating oxidant control strategies (e.g., Appendix J, smog chamber data, or an AQSM) ultimately requires a total emission inventory. The rollback-based methods generally require only a total emission value for the entire region, whereas AQSMs require, in addition, spatial and temporal resolution. Generally the major problem associated with obtaining an accurate emission inventory lies in estimating

the absolute amounts and not in estimating the spatial and temporal distribution. (The temporal distribution of emissions is, of course, more difficult to ascertain than the spatial distribution.) Thus, the additional emission resolution required by an AQSM over that required for a rollback method does not appear to introduce more serious uncertainties than those associated with estimating absolute emission levels in the first place.

ASSESSMENT OF ACCURACY OF AQSMs FOR PHOTOCHEMICAL OXIDANT

Inaccuracies in the predictions of AQSMs arise from two sources: (a) lack of complete understanding of atmospheric physics and chemistry, and (b) inaccuracies in input data due to incomplete data bases.* In terms of understanding of atmospheric physics and chemistry the primary concerns are accurate treatment of advection, turbulent diffusion, and chemistry. Although advection is a complicated process that has yet to be treated definitively, horizontal advection can be incorporated correctly in AQSMs. Inaccuracies in the treatment of horizontal advection arise largely from inaccuracies in input data, specifically wind speed and direction. Turbulent diffusion (primarily in the vertical direction) may be treated inaccurately because of a lack of complete understanding of the process. Nevertheless, most parameterizations of the vertical eddy diffusivity provide an appropriate rate of vertical mixing. Inaccuracies in our understanding of turbulent diffusion, therefore, do not appear to pose a serious problem with respect to the accuracy of predictions of AQSMs. The greatest source of uncertainty is in our understanding of the chemical transformations that lead to ozone forma-

*Liu and Seinfeld showed that an important technical limitation of AQSMs is that the diffusion equation is difficult to solve accurately (4). In particular, conventional finite difference techniques introduce a pseudo-diffusion effect as a result of poor treatment of advective transport. For example, relative errors of as much as 50 percent could be generated using the numerical method in the 1973 version of the SAI model. In general, the developers of all AQSMs have recognized this numerical problem and have implemented special techniques aimed at alleviating the undesired effect. Now discrepancies between predictions and measurements are mainly attributable to errors introduced in the formulation of the inputs to the model.

tion. These processes have been studied for many years using smog chambers, and several kinetic mechanisms have been proposed that provide concentration predictions that agree at least qualitatively with the experimental results. Yet, all the significant chemical reactions may not have been identified, and furthermore, the rate constants for many reactions believed to be important are not known very accurately. Finally, it has not been established conclusively that a mechanism validated with smog chamber data accurately represents actual atmospheric chemical processes. Initial and boundary conditions and source emissions lead to inaccuracies in predictions of AQSMs because of uncertainties due to an imcomplete data base.

In this section we attempt to assess the accuracy of AQSMs for photochemical oxidant. Recalling the discussion in the section on the Fundamentals of AQSM, we endeavor to perform here an accuracy-evaluation. Specifically, we seek to answer the question: Given the levels of uncertainty arising either from incomplete understanding of the basic physics and chemistry or from inaccurate input due to sparse data, what are the corresponding levels of uncertainty in predictions of oxidant levels? Once these levels can be ascertained (or, more precisely, estimated), then we can attempt to answer the fundamental question underlying this report, namely: At the present time are there any AQSMs sufficiently validated/evaluated and appropriate for use in designing urban oxidant control strategies?

Prior Accuracy-Evaluation Studies with AQSMs

Few of the studies present detailed sensitivity studies of model predictions to changes in input parameters. The importance of sensitivity results cannot be overemphasized. Practically they are of value in assessing the level of detail and accuracy required in model input parameters or the effects of uncertainties on predictions. The only extensive, published sensivity study for AQSMs is that of Liu et al. for the SAI model (18). Most of their findings are summarized in the following table and detailed in Table 6.

RANKING OF THE RELATIVE IMPORTANCE
OF THE INPUT PARAMETERS (SAI MODEL)

Variable	CO	NO	O_3	NO_2
Wind Speed	A	A	A	A
K_H	D	D	D	D
K_V	C	C	C	C
Mixing Depth	B	B	B	B
Radiation Intensity	D	A	A	B
Emission Rate	B	A	B	B

A — Most important

D — Least important

The effect of varying boundary and initial conditions in the 1973-version of the SAI model was reported by Demerjian (19). Average ozone concentration maps for the Los Angeles basin between the hours of 1:00 and 2:00 p.m. were presented for the base case and the case of boundary conditions reduced by 50%. Only minor differences were found at the eastern and northern edges of the basin where the maxima occur, but significant differences were observed at the western and central portions of the basin. The initial conditions in addition to the boundary conditions were reduced by 50%. Reduction in the predicted ozone levels at the northern and eastern edges of the basin was found to be of the order of 20-30% corresponding to the reduced initial conditions.

The effect of varying initial conditions in DIFKIN was studied by Demerjian. Comparative trajectory simulations were carried out for Los Angeles on September 29, 1969, for the original initial concentrations prescribed and ±20% of those values. It was found that for short time intervals the predictions are quite sensitive to the initial conditions.

Table 7 summarizes accuracy-evaluation studies carried out with the Bell Laboratories model.

TABLE 6. A SUMMARY OF THE SENSITIVITY OF THE SAI MODEL TO VARIATIONS IN INPUT PARAMETERS

Input Parameter	Variation	Local Maximum Deviation * CO ppm	Local Maximum Deviation * O_3 pphm
Wind Direction	Station measurements randomly perturbed by 0 or ±22.5°	|1.75|	
	Values at each grid point randomly perturbed by 0 or ±22.5°	|2.81|	
Wind Speed	Station measurements randomly perturbed by 0 or ±1 mph	|1.24|	
	Values at each grid point randomly perturbed by 0 or ±1 mph	|1.73|	
	Station Measurements decreased by 50%	+5.3	+43.7
	Station Measurements decreased by 25%	+2.4	+24.5
	Station Measurements increased by 25%	-2.4	-19.6
	Station Measurements increased by 50%	-4.2	-34.5
Horizontal Diffusivity	Decreased to 0	|0.04|	
(base value 50 m^2/sec)	Increased to 500 m^2/sec	| 0.3|	
Vertical Diffusivity	Decreased to 0.5 m^2/sec	+5.8	+36.3
(base value 5 m^2/sec)	Increased to 50 m^2/sec	-3.0	-16.0
Mixing Depths	Decreased by 25%	+2.6	+15.3
	Increased by 25%	-1.5	-8.5
Radiation Intensity	Decreased by 30%	0	-19.0
	Increased by 30%	0	+14.0
Emissions Rate	Decreased by 15%	-1.4	-6.3
	Increased by 15%	+1.3	+5.6

*Largest deviation from the base case at any of the N locations in the grid

TABLE 7. SENSITIVITY STUDIES WITH THE BELL LABORATORIES MODEL

Parameters varied	Results
$O(^1D)$ chemistry	$O(^1D)$ reactions were excluded from the mechanism leading to a decrease of ∿26% in the peak O_3 concentration (largely because of lower OH and lower rate of propylene-OH reaction). Conclusion - $O(^1D)$ chemistry is important in mechanisms.
Incorporation of O_3 above the mixed layer	O_3 incorporation was excluded leading to a decrease of ∿22% in the peak O_3 concentration (base case upper level O_3 concentration assumed to be 0.08 ppm.) Conclusion - Inclusion of O_3 incorporation above the mixing layer is justified. (A similar study showed incorporation of CH_4 has little effect on the calculations.)
Aerosol-radical interactions	Conclusion - Whereas aerosol-radical (primarily HO_2) stabilization of tropospheric chemistry appears realistic, its rate is too low to exert a dominant influence on the gas phase processes.
Rate constant for $OH + HO_2$	Base case $k = 2 \times 10^{-10}$ molec cm^{-3} sec^{-1}. HO_2 loss found to be controlled by the aerosol sink and not be radical chain termination. This reaction of only minor importance to OH concentrations. Conclusion - Rate constant for $OH + HO_2$ is not a vital parameter.
Aldehyde-NO_x reactions	Conclusion - Aldehyde-NO_x reactions of little consequence.

Prior Validation Studies with AQSMs

Validation (or verification) of the AQSMs with historical data is a necessary step in establishing the level of confidence that can be placed on predictions. Extensive studies have been performed with the SAI, LIRAQ, DIFKIN, and, to a lesser extent, Bell models (Table 8). There are problems in comparing the results of validation studies with different AQSMs, even for the same region, because of differences in model formulation, spatial resolution, solution procedures, and different methods of representing meteorology and chemistry. As can be seen from Table 8, the variety of regions and conditions for which the AQSMs have been validated is limited. In particular, there is a lack of validation results for widely varying emission conditions. Clearly there is a need to apply the AQSMs to different regions and under different emission conditions (e.g., weekday vs. weekend). At this time we have to rely on the results of past validation studies to draw qualitative conclusions concerning the accuracy of the AQSMs. Each of the four AQSMs has been applied to at least one urban area. Because of deficiencies in the data bases used, it is difficult to discern whether discrepancies between oxidant predictions and observations are the result of errors in the model, inaccuracies in input parameters, or deviations arising from the comparison of point data and volume-average predictions. At present none of the four AQSMs are verified to the extent desired ultimately.

Liu et al. (18) compared the SAI (1973 version) and DIFKIN model predictions for the 6 days in 1969 (20). In general, the models reproduced concentration changes of the major pollutants as a function of time reasonably well. The LIRAQ model was validated for three periods in 1973. The spatial distribution of predicted oxidant concentration compared favorably with the data for the July and August periods, although the predictions were generally lower than the station values. Predicted NO_2 values did not compare well with the data, possibly as a result of the assumed vertical profile. The LIRAQ model produced generally poor predictions for the September days; a number of possible reasons were cited, but none were quantitatively evaluated. The Bell

TABLE 8. VALIDATION STUDIES WITH AQSMs

Model	Regions	Time periods	Pollutants compared
SAI	Portions of South Coast Air Basin. Both 50x50 mi. and 80x100 mi. regions. Denver, Colo. (21)	6 days in 1969 (20) June 26, 1974 (personal communication, A. Ranzieri, 1977)	Validation studies performed with both the 15- and 31-step kinetic mechanisms. In both version, pollutants compared were NO, NO_2, O_3, CO, reactive and unreactive hydrocarbons.
LIRAQ	San Francisco Bay area. 170x210 km. region. A variety of sub-regions and grid sizes (1-5 km) were employed.	July 26, 27 August 20 September 26-28 (8) } 1973	Pollutants compared were NO, NO_2, O_3, CO, reactive and unreactive hydrocarbons.
DIFKIN	Trajectories in South Coast Air Basin	6 days in 1969 LARPP data (80)	Pollutants compared were NO, NO_2, O_3, CO, reactive and unreactive hydrocarbons.
BELL	Morris, Essex, Hudson Counties, New Jersey (Comparisons shown only for Hudson County)	May-September 1972-74. Cloudless summer weekdays with normal convective mixing and westerly winds. Only days when the integrated 06:00-13:00 solar flux was greater than 200 Langleys, average 04:00-13:00 wind velocity 6.7 mi hr^{-1} $\leq v \leq$ 10.1 mi hr^{-1}, and 04:00-13:00 wind direction was from 80° sector encompassing Essex County to the west-northwest.	O_3, NO, NO_2, SO_2. Computed O_3 behavior matches well the median of data. Computed concentration levels of second-day species agree qualitatively with levels measured in New Jersey or elsewhere (acrolein, acetaldehyde, formaldehyde, PAN, H_2O_2, HNO_2, HNO_3). Levels of HO_2 radicals estimated on the basis of predicted H_2O_2 levels. Levels of OH radicals estimated on the basis of predicted HNO_3 levels.

Laboratories model was validated against O_3 concentrations for all the days having characteristics of the hypothetical day of the simulation. Interpretation of the results of the Bell Laboratories model is difficult because the predictions apply to a region much larger than that representative of the monitoring data.

The basic problem in interpreting validation results is associated with the "tuning" of model parameters or inputs. ("Tuning" implies the adjustment of those influential parameters that are imprecisely known within their estimated upper and lower bounds to obtain as close a fit of predicted and observed concentrations as possible.) In most serious validation studies, all model parameters and inputs are determined *a priori* based on the conditions of the simulation and are not adjusted to modify the predictions. Nevertheless, there are usually certain inputs, for example initial concentrations aloft and boundary concentrations aloft, that are simply not available and must be estimated. These concentrations, particularly the concentrations aloft during the day, are often adjusted to obtain as good a fit as possible. Kinetic rate constants and turbulent diffusivities are generally not adjusted nor are the calculated wind and inversion fields. The key issue is the sensitivity of the predictions to those inputs that are adjusted. If the predictions are highly sensitive, for example, to the assumed ozone concentration at the inversion base, and that concentration is unknown, it would be difficult to place considerable confidence in the predictions of the model. If, on the other hand, the assumed ozone concentration aloft has only a mild influence on the predicted ozone and ozone aloft is the only adjusted parameter, then one is safe in placing confidence in the predictions.

We have chosen not to present here extensive examples of the comparison of predicted and observed oxidant concentrations from prior validation studies for the four AQSMs. Such comparisons are, of course, available in the primary references. A particularly noteworthy validation study is that recently carried out by SAI for the Denver airshed with the current version of the SAI model (21). The work is noteworthy

in that it is the first significant verification study carried out with the SAI model for a region other than the South Coast Air Basin and the first major verification study of the current version of the SAI model.

Figures 1-3 show comparisons of predicted and observed ozone concentrations at each of the monitoring stations on July 29, 1975, July 28, 1976, and August 3, 1976, respectively. Figure 4 shows the variation of averages over all stations of observations and predictions. Finally, Figure 5 presents the correlation of observed and predicted ozone levels for the three validation days at nine stations.

To obtain the results of Figures 1-5, very little parameter tuning was reported. Aldehyde photolysis rates were adjusted slightly based on prior trajectory simulations; likewise, initial and boundary conditions were changed somewhat, although the adjustments in I.C. and B.C. had less than a 1 pphm effect on the O_3 levels predicted. The upper-level concentration of O_3 was assumed to be background (0.02 ppm) and was not varied during the simulations. Thus, these results appear to reflect the capability of one AQSM in the absence of parameter adjustment. From these results a level of accuracy of ±50%, and in several cases a much lower value, is evident.

Accuracy of AQSMs

In this section we address the question: How accurate are the current AQSMs? Ideally one would attempt to answer this question through detailed accuracy-evaluation studies. In these studies uncertainty limits on the important input parameters would be prescribed. Through the exercising of the model these input uncertainties would be translated into uncertainties in predicted oxidant. Time did not permit such a study for the purposes of this report. Thus, based on an analysis of the uncertainties associated with key input parameters, we hope to indicate qualitatively whether any of the AQSMs can predict oxidant levels with an accuracy necessary for control strategy evaluation. Also

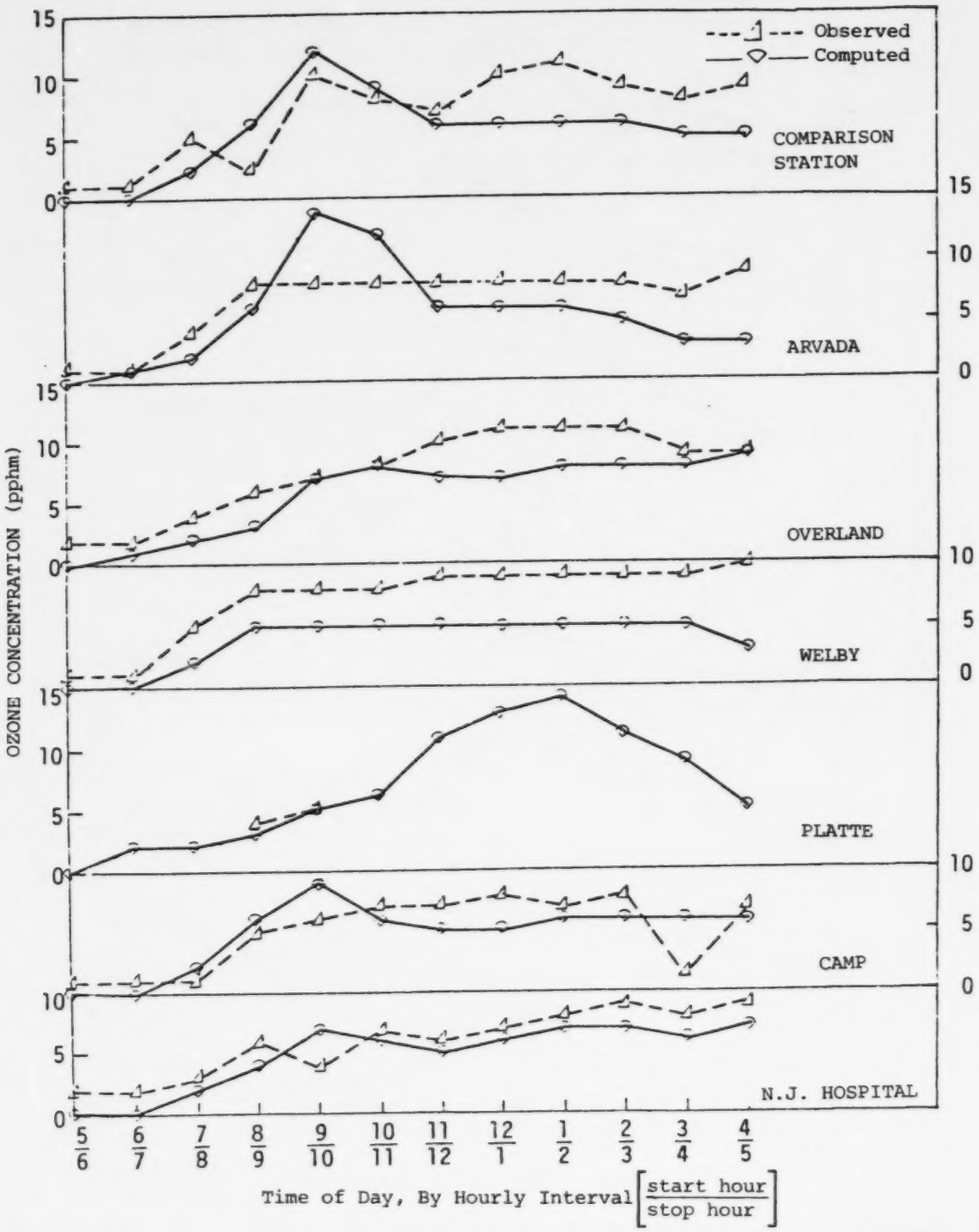

Figure 1. Denver air quality model validation comparisons for 29 July 1975.

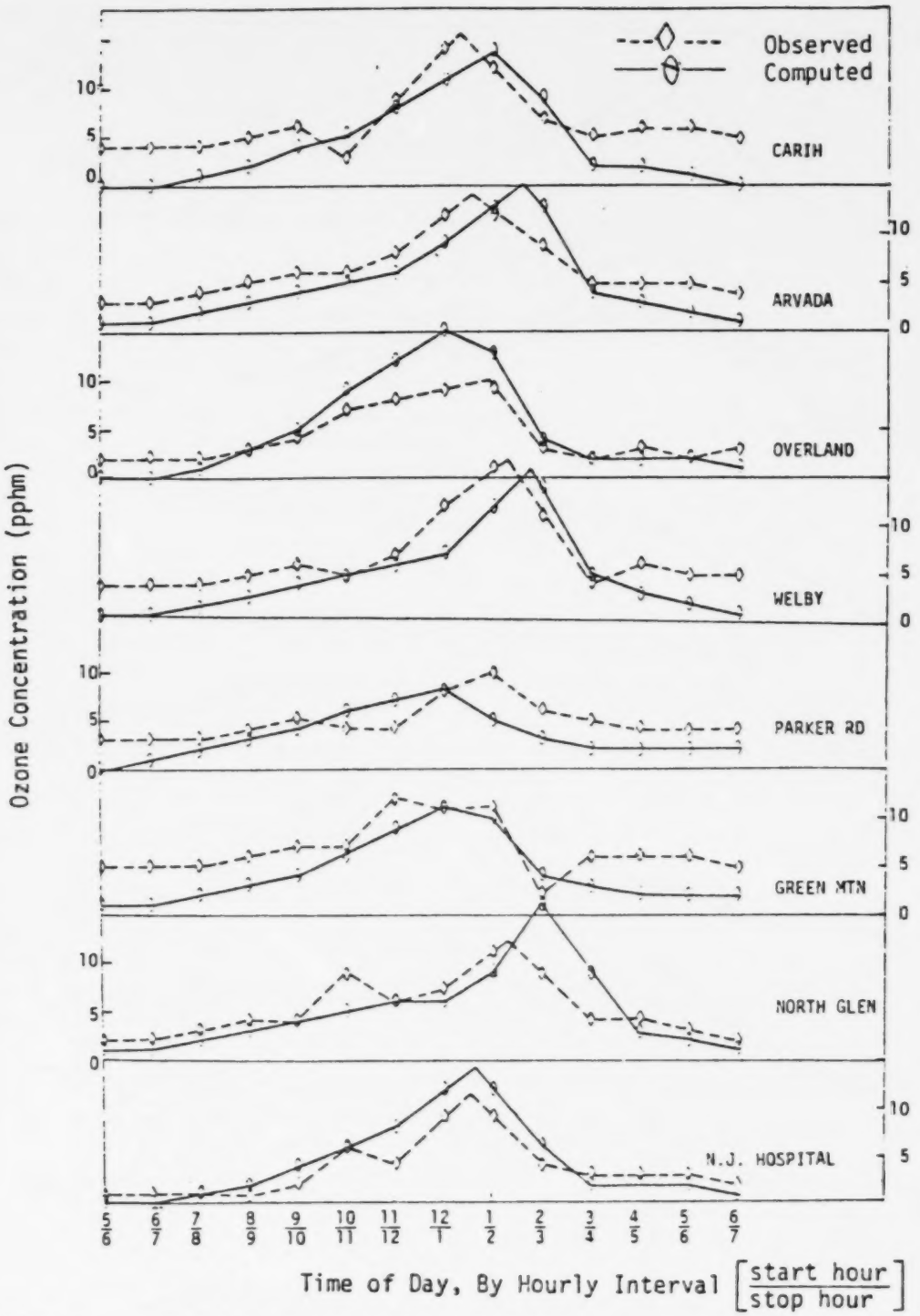

Figure 2. Denver air quality model validation computed/observed comparison at various stations for 28 July 1976.

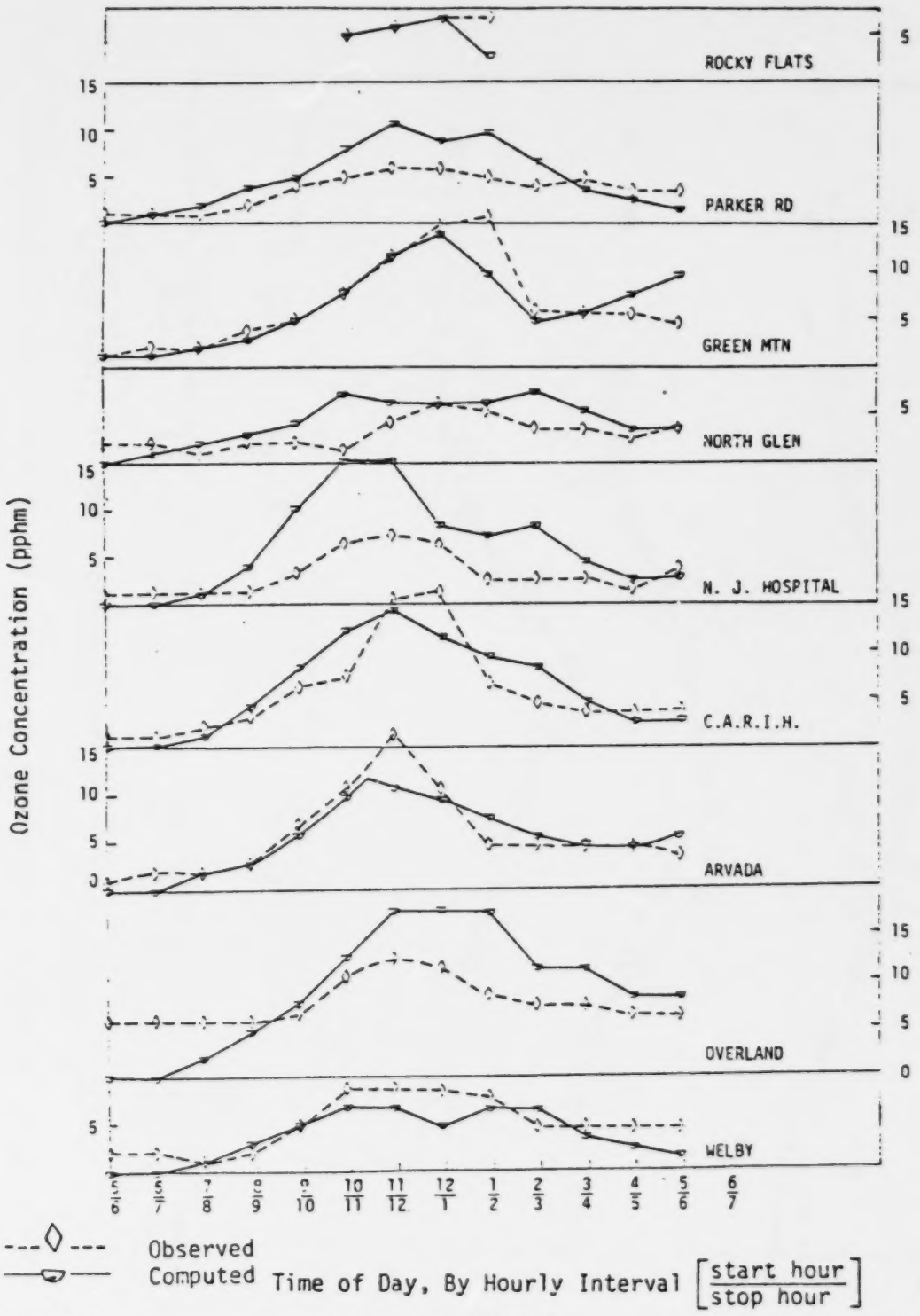

Figure 3. Denver air quality model validation computed/observed comparison at various stations 3 August 1976.

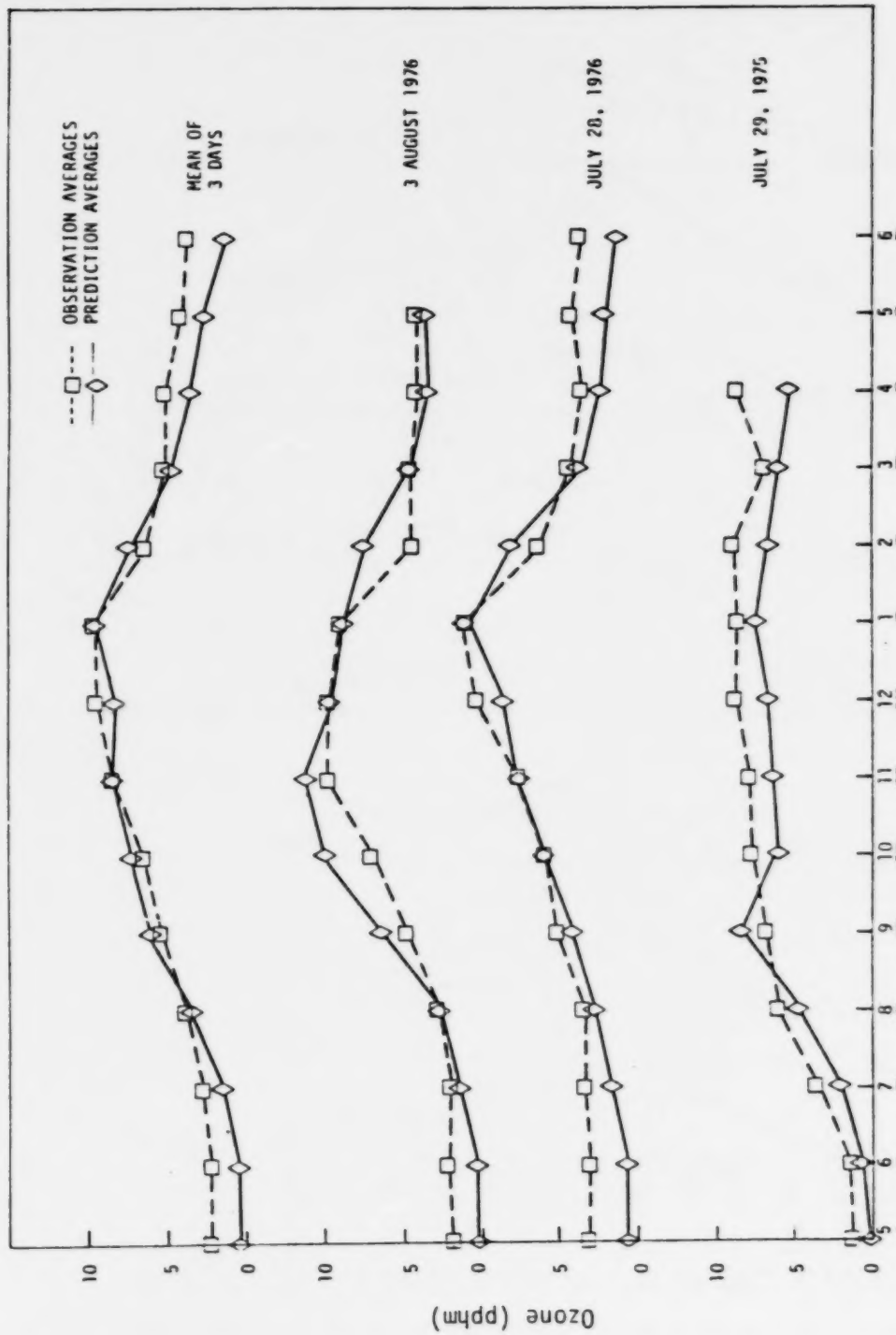

Figure 4. The variation of averages over all stations of observations and predictions.

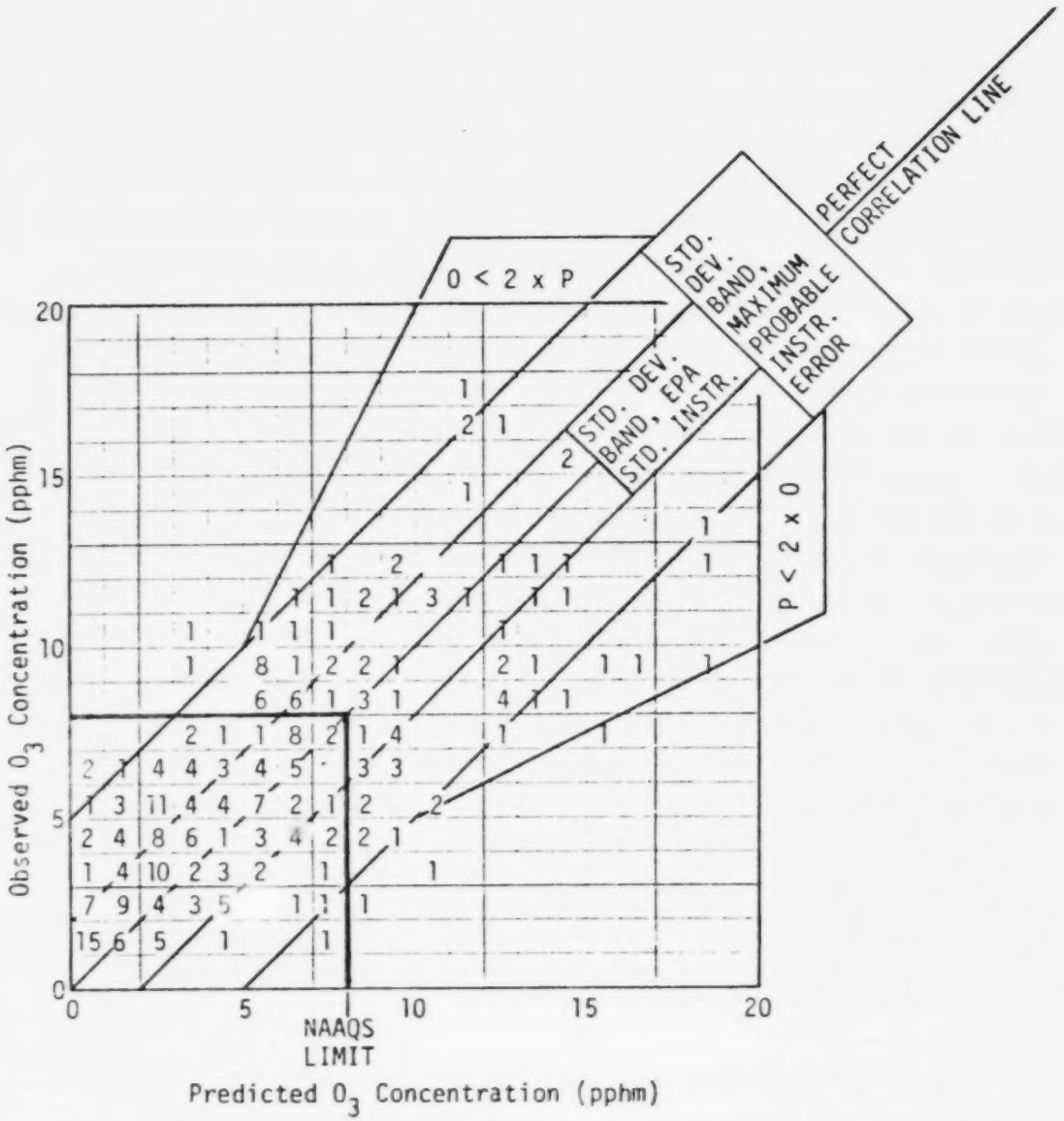

Figure 5. Denver air quality model validation computed/observed correlations (data for 3 days, 9 stations, daylight hours).

we will compare the four AQSMs in an attempt to determine which, if any, of the four are to be preferred.

An important aspect of an AQSM is a proper balance among the degrees of detail of the treatments of the main chemical and physical processes. The Bell Laboratories model is the only one of the three that does not involve any vertical resolution in the concentration distributions; and, of course, the Bell Laboratories model involves the most detailed chemical treatment of the four AQSMs. The important issue in this regard that must be faced is, therefore: What degree of vertical resolution is consistent with the representation of prevailing chemical processes? If instantaneous vertical mixing up to an inversion base height is assumed, then for this assumption to be valid, the characteristic time scale of the chemical reaction processes must be long when compared to the time scale for vertical mixing so that the chemical reaction rates based on vertically integrated concentrations are essentially equal to the vertically integrated chemical reaction rates based on the local concentrations. An analysis of this question is presented in the Appendix. The conclusion drawn from the analysis in the Appendix is that assumed instantaneous mixing in the layer between the ground and an inversion base is inconsistent with a treatment of chemistry as detailed even as that in the SAI and LIRAQ models. We, therefore, conclude that:

- Because of the inconsistency between the levels of detail of the representations of chemistry and transport, the Bell Laboratories model is not viewed as a likely candidate for oxidant prediction when compared to the other three models that contain vertical resolution.

Because of the specialized nature of DIFKIN as a trajectory model, this model is not viewed as strong a candidate for general oxidant prediction as the two grid-based models. With the inclusion of a better chemical mechanism in DIFKIN, it will serve as a useful tool for special studies for which a trajectory model is appropriate.

As we noted, we would like to translate uncertainties in input parameters into uncertainties in predicted oxidant levels. If we summarize uncertainties estimated in this section we have:

• Chemical kinetics (Ozone levels)	±50%
Initial concentrations (HNO_2, aldehydes)	
Rate constants	
Mechanisms of hydrocarbon oxidation	
• Meteorology	
Wind speeds and directions	±20%
Mixing depth	±25%
Light intensity	±20%
• Initial and Boundary Conditions	±50%
Initial concentrations aloft	
Boundary concentrations aloft	
• Emission Inventories	
NO_x	±20%
Hydrocarbons	±30%

In the absence of detailed accuracy evaluation studies, an estimate of the uncertainty in predicted ozone levels as a result of the above input uncertainties acting individually or in concert represents sheer guesswork. In the Appendix we have singled out two of the most influential uncertainties, namely initial concentrations of radical-producing species and the upper level boundary conditions, together with the question of the degree of vertical resolution for more detailed study. On the basis of the Appendix and of the prior validation studies cited in the previous section, one is inclined to place an overall uncertainty on oxidant level predictions from current AQSMs of ±50%. We therefore conclude that:

- Oxidant level predictions of current grid-based AQSMs (i.e., the SAI and LIRAQ models) have an estimated uncertainty of ±50%.

CONCLUSIONS AND RECOMMENDATIONS

In this report we have attempted to estimate the level of accuracy associated with the oxidant predictions of current AQSMs. The question we have intended to address is:

- At the present time are there any AQSMs sufficiently validated/evaluated and appropriate for use in designing urban oxidant control strategies?

It is clear that it is difficult to provide an unequivocal answer to this question, since one must eventually compare AQSMs with other methods available for oxidant prediction and select the method most compatible with the intended use of the method and the available data. Since this report has not analyzed other oxidant prediction methods, we cannot provide a recommendation on which method should be used under which circumstances. The aspect we must consider is: In light of the accuracy of AQSM oxidant predictions estimated in the preceding section, do we consider these AQSMs "sufficiently validated/evaluated?"

It seems that AQSMs for photochemical oxidant have reached a level of detail wherein major new chemical or physical changes are unlikely. There are inherent uncertainty limits that will be difficult to reduce. These are the result of the need to represent chemistry in a relatively concise manner and of the lack of availability of all the required inputs. We have estimated the current level of uncertainty in *absolute* levels of oxidant predictions as approximately ±50%. It is anticipated that the uncertainties associated with representing *relative* changes in oxidant levels is somewhat smaller than ±50%.

In terms of the four AQSMs surveyed we arrived at the following conclusion:

- Of the four AQSMs surveyed, the SAI and LIRAQ models are deemed most appropriate for use in designing urban oxidant control strategies.

The final question of interest is: Should AQSMs be recommended over existing methods for oxidant prediction? Obviously this question cannot be answered in the absence of a comparative study of the available methods. It seems clear, however, that *AQSMs represent ultimately the preferred procedure for oxidant prediction.* We offer the following recommendation:

- A comparative study of the SAI and/or LIRAQ models with the chamber data of Dimitriades (22, 23) be carried out relative to their utility and accuracy as techniques for designing urban oxidant control strategies.

Even in the absence of detailed comparative studies, it seems safe to conclude that either chamber data or AQSMs are more representative of atmospheric phenomena than is the Appendix J curve. With such a study as recommended above it would be hoped to establish which of the two is the most useful at this time.

APPENDIX A. EVALUATION OF KINETIC MECHANISMS

In principle, every reaction appearing in a photochemical smog mechanism is subject to some degree of uncertainty, whether in the rate constant or the nature and quantity of the products. In validating a mechanism, the accepted procedure is to compare the results of smog chamber experiments, usually in the form of concentration-time profiles, with simulations of the same experiments using the proposed mechanism. A sufficient number of experimental unknowns exist in all such mechanisms so that the models can be "tuned" to fit most experimental data. The inherent validity or accuracy of any mechanism should be judged on the basis of this tuning procedure by evaluating how realistic the proposed parameter variations are.

Uncertainties in the kinetic mechanism are related to inaccurately known rate constants or products for reactions in the mechanism. Uncertainties associated with comparison of the predictions of the mechanism to experimental smog chamber data arise, in addition, because the properties of the photochemical reactor, associated equipment, and experimental procedures are not completely known.

In this Appendix we discuss kinetic mechanisms for photochemical smog. We focus particularly on those important aspects of mechanisms that have some degree of uncertainty at present. Our object is to assess the expected level of accuracy of prediction of current kinetic mechanisms.

Inorganic Chemistry

The inorganic reactions important in photochemical smog are, by and large, well established. Rate constant values for a number of the inorganic reactions have been revised from earlier values as new determinations have been carried out. The primary photochemical cycle of NO_2-NO-O_3 is well established and need not be discussed. Aside from the primary photochemical cycle, the most important inorganic reactions are

those involving hydroxyl and hydroperoxyl radicals and nitrous and nitric acids. Rate constant values for reactions involving OH and HO_2 are difficult to determine, and there is still considerable uncertainty associated with several of them. Table A-1 summarizes recent rate constant determinations for the important inorganic reactions involving OH, HO_2, HNO_2, and HNO_3.

TABLE A-1. SELECTED INORGANIC REACTIONS

Reaction	Rate Constant @25°C (ppm, min Units)	Reference
1. $NO + OH \rightarrow HONO$	1.6×10^4	(24) (25)
2. $NO_2 + OH \rightarrow HONO_2$	1.6×10^4	(26)
3. $NO + HO_2 \rightarrow NO_2 + OH$	1.5×10^3 1.8×10^3 1.2×10^4	(27) (28) (29)
4. $NO_2 + HO_2 \rightarrow HO_2NO_2$	1.2×10^3 [a]	(30)
5. $NO_2 + HO_2 \rightarrow HONO + O_2$	< 4.5	(30)
6. $HO_2NO_2 \rightarrow HO_2 + NO_2$	2-14 min^{-1}	(31)

[a] Estimated based on ratio of rate constants, $(k_4 + k_5)/k_3 = 0.1$, as found by Simonaitis and Heicklen (27). Howard (30) has reported a low pressure (third order) value of k_4 but extrapolation to 1 atm. is not possible.

The very recent determination of k_3 by Howard and Evenson (29) necessitates reevaluation of the influence of Reaction 3 on predictions of mechanisms. Reaction 3 has always been very influential in the conversion of NO, NO_2, and, with a new value of k_3 almost an order of magnitude higher than the previously used value, its influence may be even more substantial.

Olefin Chemistry

Olefin-OH· Reactions--

The olefin-OH· reaction is well established as a key reaction in photochemical smog. The mechanism of the olefin-OH· reaction for the common olefins is largely agreed upon, and rate constant values are reasonably certain. The ethylene-OH· reaction is thought to proceed as follows:

$$CH_2 = CH_2 + OH\cdot \xrightarrow{O_2} CH_2(OO\cdot)CH_2OH \qquad 1.33 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1} \qquad (32)$$

Subsequent steps in the presence of NO_x are (these reactions will be discussed subsequently):

$$CH_2(OO\cdot)CH_2OH + NO \longrightarrow NO_2 + CH_2(O\cdot)CH_2OH$$

$$CH_2(O\cdot)CH_2OH \longrightarrow HCHO + \cdot CH_2OH$$

$$\cdot CH_2OH \xrightarrow{O_2} HCHO + HO_2\cdot$$

The main product of the ethylene-OH· reaction is, therefore, formaldehyde.

The propylene-OH· reaction is currently thought to proceed by two paths, addition and abstraction:

$$CH_3CH = CH_2 + OH\cdot \xrightarrow{O_2} CH_3(OO\cdot)CHCH_2OH$$

$$\xrightarrow{O_2} CH_2(OO\cdot)CHCH_2 + H_2O \qquad 3.8 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1} \qquad (33)$$

$$CH_3(OO\cdot)CHCH_2OH + NO \rightarrow NO_2 + CH_3(O\cdot)CHCH_2OH$$

$$CH_3(O\cdot)CHCH_2OH \rightarrow CH_3CHO + \cdot CH_2OH$$

$$\cdot CH_2OH \xrightarrow{O_2} HCHO + HO_2\cdot$$

After the initial reaction, either an hydroxy-peroxyalkyl or a peroxyalkyl radical is formed, leading, after reaction with NO, to a hydroxy-alkoxyl or an alkoxyl radical. The likely reaction paths of these radicals will be discussed.

Olefin-O_3 Reactions--

The possible mechanisms of olefin-O_3 reactions were elucidated by O'Neal and Blumstein (34). The propylene-O_3 reaction is currently thought to proceed as follows:

$$CH_3CH = CH_2 + O_3 \xrightarrow{O_2} \begin{cases} HCO_3\cdot + CH_3CHO + OH\cdot \\ HCHO + CH_3C(O)O_2\cdot + OH\cdot \end{cases}$$

Rate constants for olefin-ozone initiation steps are reasonably well established. The principal areas of uncertainty in olefin-ozone chemistry are: (a) the extent of stable ozonide formation, and (b) the split between each of the two paths, as shown above. In propylene photooxidation experiments, measurement of the acetaldehyde/formaldehyde ratio aids in establishing the importance of each of the two reaction paths.

Paraffin Chemistry

The main oxidation reaction of paraffins is with hydroxyl radicals. The products of reaction between paraffins and OH· in air are a peroxyalkyl radical and water. For butane, for example, hydroxyl radicals can abstract a hydrogen from either the primary or secondary carbon as follows:

$$C_4H_{10} + OH\cdot \xrightarrow{O_2} \begin{cases} CH_3CH_2CH_2CH_2OO\cdot + H_2O \\ CH_3CH_2\underset{\displaystyle OO\cdot}{\underset{|}{C}}HCH_3 + H_2O \end{cases}$$

The peroxyalkyl radicals react with NO to produce NO_2 and alkoxyl radicals. Because alkoxyl radicals can thus be viewed as the effective product of the paraffin-OH· reaction, alkoxyl radicals play an essential role in the chemistry of paraffin systems.

Aldehyde Chemistry

It is now well established that aldehydes play an extremely important role in smog chemistry. Aldehydes participate in the reaction process in two ways: (a) photolysis to give stable products and radicals, and (b) reaction with hydroxyl radicals to give acyl radicals that are rapidly converted to peroxyacyl radicals. The detailed chemistry of aldehydes is still somewhat uncertain because of uncertainties in aldehyde photolysis rates and in rate constants for aldehyde-OH· reactions.

Formaldehyde Chemistry--

Photolysis of formaldehyde leads to hydrogen atoms and formyl radicals:

$$HCHO + h\nu \rightarrow H\cdot + HCO\cdot$$

The hydrogen atoms immediately form hydroperoxyl radicals. The possible paths for reaction of the formyl radical are:

$$HCO\cdot + O_2 \begin{cases} \xrightarrow{a} HCO_3\cdot \\ \xrightarrow{b} HO_2\cdot + CO \\ \xrightarrow{c} OH\cdot + CO_2 \end{cases}$$

Quantum yields as a function of wavelength for formaldehyde photolysis are highly uncertain. At longer wavelengths formaldehyde photolysis proceeds as:

$$HCHO + h\nu \rightarrow H_2 + CO$$

Osif and Heicklen (35) estimated the ratio of the rates of paths a and b to be 5 and the ratio of the rates of paths c and b to be less than 0.2. The peroxyformyl radical will react with NO as follows:

$$HCO_3\cdot + NO \xrightarrow{O_2} NO_2 + HO_2\cdot + CO_2$$

Note that path a results in the net conversion of two molecules of NO to NO_2, whereas path b leads to only a single NO to NO_2 conversion. Thus, the split between paths a and b influences ozone formation.

The reaction of formaldehyde with hydroxyl radicals proceeds as follows:

$$HCHO + OH\cdot \rightarrow HCO\cdot + H_2O \qquad 2.2 \times 10^4 \text{ ppm}^{-1}\text{min}^{-1} \qquad (36)$$

Formaldehyde photolysis and reaction with OH· lead to the formyl radical. Further elucidation of the fate of the formyl radical is an important need in determining formaldehyde chemistry.

Acetaldehyde Chemistry--

The principal acetaldehyde reactions are:

$$CH_3CHO + h\nu \xrightarrow{O_2} CH_3O_2\cdot + HCO_3\cdot$$

$$CH_3CHO + OH\cdot \xrightarrow{O_2} CH_3C(O)O_2\cdot + H_2O \qquad 2.2 \times 10^4 \text{ ppm}^{-1}\text{min}^{-1} \qquad (37)$$

Peroxy Radical Chemistry

Peroxy radical chemistry forms the basis for the production of ozone and organic products. Because of the difficulties associated with measurement of rate constants of reactions involving peroxy radicals, there is still a considerable degree of uncertainty concerning peroxy radical reactions.

Reactions of Alkoxyl Radicals with Oxygen and Thermal Decomposition--

Two possible reaction paths for the alkoxyl radical are decomposition and reaction with molecular oxygen. It is now established that the decomposition of the shorter chain alkoxyl radicals is unimportant compared to the reaction of the shorter chain alkoxyl radicals with molecular oxygen (38, 39). Barker et al. have shown that the rate constants for alkoxyl radical-O_2 reactions are almost independent of the size of the radical (39). Unimolecular decomposition rates, on the other hand, increase rapidly with increasing size of the radical. Thus, as the alkyl group increases in size, at some point unimolecular decomposition becomes competitive with reaction with O_2. The point at which the two rates become equal has not been firmly established.

The reaction of methoxyl radicals with O_2 is:

$$CH_3O\cdot + O_2 \rightarrow HCHO + HO_2\cdot \qquad 0.9\ ppm^{-1}min^{-1} \qquad (38,39)$$

Decomposition of the methoxyl radical is negligible when compared to the above reaction. The sec-butoxyl radical formed in the photooxidation of butane undergoes decomposition or oxygen addition as follows:

$$CH_3CH_2\overset{O\cdot}{\underset{|}{C}}HCH_3 \xrightarrow{O_2} CH_3CH_2O_2\cdot + CH_3CHO$$

$$CH_3CH_2\overset{O\cdot}{\underset{|}{C}}HCH_3 + O_2 \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3 + HO_2\cdot$$

The relative importance of these two paths has not been established but can be inferred from the relative amounts of methyl ethyl ketone, butyraldehyde, and acetaldehyde formed in a butane photooxidation. The primary butoxyl radical probably does not decompose but reacts with oxygen.

Hydroxy-alkoxyl radicals are formed in the olefin-OH· reaction. For example, in propylene photooxidation we obtain the hydroxy-alkoxyl radical through the reaction

$$CH_3\overset{OO\cdot}{\underset{|}{C}}HCH_2OH + NO \rightarrow NO_2 + CH_3\overset{O\cdot}{\underset{|}{C}}HCH_2OH$$

Although the fate of this radical is not known precisely, it is generally felt at this time that unimolecular decomposition occurs exclusively:

$$CH_3\overset{O\cdot}{\underset{|}{C}}HCH_2OH \rightarrow CH_3CHO + \cdot CH_2OH$$

Because of the importance of the olefin-OH· reaction, uncertainties in the fate of the hydroxy-alkoxyl radical will introduce uncertainties in overall kinetic mechanisms.

Reactions of Peroxy Radicals with NO and NO_2--

Conversion of NO to NO_2 occurs primarily by reactions of the form

$$RO_2\cdot + NO \rightarrow NO_2 + RO\cdot$$

Aside from the $HO_2\cdot$-NO reaction, rate constant values have not been measured for the peroxyalkyl-NO reactions. Darnall et al. (40) have postulated that longer chain peroxyalkyl radicals (C_{4+}) will add to NO to form an excited complex:

$$RO_2\cdot + NO \rightarrow RO_2NO$$

$$RO_2NO \rightleftharpoons RONO_2$$

$$RONO_2 \xrightarrow[M]{a,\,b} RO\cdot + NO_2 \quad (a)$$
$$\qquad\qquad\quad \rightarrow RONO_2 \quad (b)$$

Darnall et al. estimated the ratio k_a/k_b to be 0.09 for butyl, 0.16 for pentyl, and 0.6 for hexyl systems (40).

Peroxyalkyl-NO_2 reactions have been studied by Simonaitis and Heicklen (27). They reported that the ratio of the rate constants for RO_2-NO and RO_2-NO_2 reactions is 2.2. The peroxyalkyl-NO_2 reaction may proceed by:

$$RO_2\cdot + NO_2 \rightarrow \begin{cases} RO_2NO_2 \\ R'CHO + HNO_3 \end{cases}$$

Simonaitis and Heicklen reported that production of the alkylperoxynitrate occurs 75 percent of the time (27). For methylperoxy, for example,

$$CH_3O_2\cdot + NO_2 \rightarrow \begin{cases} CH_3O_2NO_2 \\ HCHO + HNO_3 \end{cases}$$

The peroxynitrate may react with NO_2 to produce methyl nitrate or with NO to give methyl nitrite (41). As in the case of the HO_2-NO_2 reaction, the RO_2-NO_2 reaction diminishes the formation of ozone. At this time the mechanism (and rate constants) of the RO_2-NO_2 reaction is largely uncertain. Because of its importance in ozone formation, this reaction should be studied further.

The primary pathway of alkoxyl-NO reactions is (42):

$$RO\cdot + NO \rightarrow RONO \qquad 4.9 \times 10^4 \text{ ppm}^{-1}\text{min}^{-1}$$

The alkyl nitrite will photolyze to give back the alkoxyl radical and NO. The photolysis rates of the nitrites are, however, uncertain. Since alkyl nitrites represent a reservoir for NO_x, uncertainty in the photolysis rates of the alkyl nitrites leads to uncertainties in the overall photooxidation chemistry.

Two reaction paths for the alkoxyl-NO_2 reaction have been reported (38,39):

$$RO\cdot + NO_2 \xrightarrow{a} RONO_2$$

$$\xrightarrow{b} RCHO + HNO_2$$

Barker et al. (39) estimated the ratio k_b/k_a to be 0.3, whereas Baker and Shaw (43) and Wiebe et al. (44) estimated $k_b/k_a = 0.11$. Mendenhall et al. (38) determined the rate constant for $RO\cdot + NO_2$ as 7.8×10^3 ppm^{-1} min^{-1}, and Barker et al. found the rate constant to be 1.55×10^4 ppm^{-1} min^{-1} (39). Thus, the rate constant is uncertain by about a factor of two. In addition, there is some uncertainty as to the split between the two reaction paths shown above. The split is important since path a removes both a free radical and an NO_x, whereas path b returns a hydroxyl radical from the subsequent photolysis of nitrous acid.

The competition between NO and NO_2 for peroxyacyl radicals is an important factor in both PAN and ozone formation. For peroxyacetyl radicals, for example:

$$CH_3\overset{O}{\overset{\|}{C}}OO\cdot + NO \xrightarrow{a} NO_2 + CH_3\overset{O}{\overset{\|}{C}}O\cdot \qquad 4 \times 10^3 \qquad (45)$$

$$CH_3\overset{O}{\overset{\|}{C}}OO\cdot + NO_2 \xrightarrow{b} CH_3\overset{O}{\overset{\|}{C}}OONO_2 \text{ (PAN)} \qquad 2.09 \times 10^3 \qquad (45)$$

Radical-Radical Reactions--

The reactions of peroxyalkyl and peroxyacyl radicals with $HO_2\cdot$ provide a sink for free radicals.

$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad 8.3 \times 10^3 \text{ } ppm^{-1}min^{-1} \qquad (46)$$

$$RO_2\cdot + HO_2\cdot \rightarrow ROOH + O_2$$

$$RC(O)O_2\cdot + HO_2\cdot \rightarrow RC(O)OOH + O_2$$

In addition, peroxyalkyl-peroxyalkyl reaction may be a source of alkoxyl radicals:

$$RO_2\cdot + RO_2\cdot \rightarrow 2RO\cdot + O_2$$

A rate constant value of about 500 $ppm^{-1}min^{-1}$ for the methylperoxy recombination was reported by Parkes et al. (47), Whitbeck et al. (48), and Hochanadel et al. (49).

Because of the experimental difficulties associated with measurement of radical-radical reaction rate constants, at present the rate constants of the above reactions are not available in general and must be estimated. Since these reactions control the size of the overall radical pool, they are important in kinetic simulation.

PAN Chemistry

The PAN formation reaction was given the section on Reactions of Peroxy Radicals with NO and NO_2. Pate et al. (50) suggested that PAN decomposes as follows:

$$CH_3\overset{O}{\overset{\|}{C}}OONO_2 \rightarrow CH_3\overset{O}{\overset{\|}{C}}OO\cdot + NO_2 \qquad 0.0372\ min^{-1} \qquad (45)$$

PAN concentrations are controlled by the competition between NO and NO_2 for peroxyacyl radicals and by PAN decomposition. The peroxyacyl-NO reaction is given in a preceding section. The acetyl radical resulting from that reaction decomposes as follows:

$$CH_3CO_2\cdot \xrightarrow{O_2} CH_3O_2\cdot + CO_2$$

so that the result of the competition strongly influences ozone production.

Aromatic Chemistry

The lack of understanding of aromatic chemistry represents one of the most serious weaknesses in our overall knowledge of the photochemical smog system. Hansen et al. (51) and Hendry* have recently measured rate constants of reactions involving aromatic hydrocarbons and hydroxyl radicals. (Reaction of aromatics with atomic oxygen is slow and can presumably be neglected.) A value of 1×10^4 $ppm^{-1}min^{-1}$ for the toluene-OH· reaction is consistent with the results of both groups. Toluene is the aromatic species most studied.

Hendry has suggested that the main pathway is addition of OH· to the rather than abstraction of a hydrogen from the methyl group because of the similarity of the toluene-OH· rate constant to those of other alkyl benzene-OH· reactions.

Schwartz (52) reported nitrotoluene and aerosol formation in toluene photooxidation experiments. Akimoto et al. (53) found o-cresol, α-nitro-toluene, and m-nitrotoluene resulting from the toluene-OH· reaction.

The mechanism of aromatic-OH· reactions is largely speculation at this time. As noted, this mechanism represents an important area of uncertainty in kinetic simulations.

Generalized Mechanisms

The key issue in the use of a generalized mechanism is the selection of the organic species to be included within each lumped class. In the original Hecht et al. (7) mechanism (see Table 3) each lumped species represents a different hydrocarbon class. The rate constants corresponding to each class are to be determined as average rate constants

*Private communication from D.G. Hendry to G.Z. Whitten, 1976.

calculated on the basis of the composition of the class. A problem with this approach is that it is difficult to represent high concentrations of less reactive species and low concentrations of highly reactive species in the same class with one set of rate constants. As the reaction proceeds, the more reactive species are preferentially depleted first, and the effective lumped rate constants change with time. Thus, when employing a lumped mechanism it is desirable to collect species that not only behave mechanistically similarly but also have roughly the same reactivity.

As noted earlier, Whitten and Hogo (9) have suggested a somewhat different interpretation for the lumped reactant classes in the Hecht et al. mechanism. In that mechanism, termed the Carbon Bond Mechanism, each carbon atom is treated according to its bond type. Organics are divided into four groups: (a) single-bonded carbon atoms (paraffins and the single-bonded carbon atoms of olefins, aromatics, and aldehydes), (b) fast double bonds (olefins excluding ethylene), (c) slow double bonds (ethylene and aromatics), and (d) carbonyl bonds. Aside from the inclusion of new information on several reactions, the principal change from the Hecht et al. mechanism is that ethylene, the least reactive olefin, is included with aromatics in the class of slow double bonds.

Summary of Uncertainties in Kinetic Mechanisms

The concentrations predicted by the kinetic mechanism are extremely sensitive to the values of several reaction rate constants. Reactions which are particularly sensitive are those governing the conversion of NO to NO_2,

$$NO + HO_2 \rightarrow NO_2 + OH$$

$$NO + RO_2 \rightarrow NO_2 + RO$$

and the reactions which initiate the oxidation of olefins,

O_3 + olefins → radicals + stable products

OH + olefins → radicals + stable products

Hecht and Dodge performed a systematic sensitivity analysis on all the reactions in the original Hecht-Seinfeld-Dodge lumped kinetic mechanism (13). The conclusions of the study were compiled in the form of a ranking of the reactions by their "sensitivity-uncertainty" index. This index is an indicator of the combined sensitivity of the mechanism to variations in the reaction rate constant and the experimental uncertainty of the rate constant. Since this study was performed, only a few rate constant determinations have been significantly improved. However, a number of previously accepted kinetic data are currently in dispute. For example, the reaction of NO_2 with HO_2 is now suspected of being an addition reaction to form peroxynitric acid, HO_2NO_2, rather than a pathway for forming nitrous acid, HONO, and O_2.

Since urban smog is initiated photochemically, kinetic mechanisms must be able to predict the photolysis rates of pollutants that absorb ultraviolet light. From Beer's Law, in an optically thin medium, the "rate constant" governing the photolysis rate of a compound is given by:

$$k = \frac{1}{(\lambda_2-\lambda_1)} \int_{\lambda 1}^{\lambda 2} \phi(\lambda) I_o(\lambda) \varepsilon(\lambda)\, d\lambda$$

where: $I_o(\lambda)$ is the incident light intensity distribution
$\varepsilon(\lambda)$ is the extinction coefficient
$\phi(\lambda)$ is the primary quantum yield
λ_1 and λ_2 are the wavelength limits of the light reaching the urban atmosphere.

The photolysis rate of the absorbing species is then,

Rate = kc

where c is the concentration of the absorbing species.

In smog chamber simulations, the photolysis rate is usually expressed in terms of k_1, the rate constant for NO_2 photolysis. From this, with information on $I_o(\lambda)$, $\varepsilon(\lambda)$, and $\phi(\lambda)$, photolysis rates of other species can be predicted. Considerable uncertainty exists in the measurement of $\phi(\lambda)$ for certain species. For instance, the photolysis of ozone can be important in the formation of OH radicals. In the wavelength region of interest, the primary quantum yields for the processes

$$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D)$$

$$O_3 + h\nu \rightarrow O_2(^1\Sigma) + O(^3P)$$

are still uncertain. While extinction coefficients are relatively easy to measure in the laboratory for most species, quantum yield measurements can be exceedingly difficult.

Another important photochemical process is the formation and subsequent reaction of excited states. The rates of thermal reactions can be enhanced by several orders of magnitude if one or more of the reactants are vibrationally or electronically excited. For instance while ground state $O(^3P)$ atoms are unreactive toward such species as H_2, H_2O, and N_2O, singlet oxygen, $O(^1D)$, reacts rapidly. Similarly, the oxidation of SO_2 in clean air probably takes place by the reaction of triplet $SO_2(^3SO_2)$ formed by the absorption of UV light by ground state SO_2 followed by internal energy transfer processes. $^3SO_2$ may also be considerably more reactive toward hydrocarbons than the ground state SO_2. Unfortunately, both the formation and reaction mechanisms of most electronically excited species are highly uncertain.

In summary, of all the unknowns in the homogeneous chemistry of photochemical smog, the processes most often parameterized are:

- the rates of reaction of RO_2 with NO;
- rates of reaction and mechanisms of oxidation of the olefins, aromatics and alkanes, i.e., numbers and types of radicals formed;
- relative rate constants for the photolysis of absorbing species such as O_3 and HONO.

The second major set of unknowns in photochemical smog mechanisms concerns the effects of smog chambers on the observed chemical processes. Since mechanisms must be validated using smog chamber data, the characteristics of the chamber must be built into the model explicitly. Some of the specific effects or characteristics that must be considered are: the spectral distribution and absolute intensity of the photolyzing lamps; the absorption, desorption, and chemical reaction of species on the walls; the initial loading of impurity species in the chamber on the walls or in the gas; and the effects of leakage, sampling, and possible temperature variations during the run. Of these effects, probably the most important are the properties of the photolysis lamps. Photolysis rates of absorbing species cannot be predicted with accuracy if $I_o(\lambda)$, the incident light intensity distribution, is not known with accuracy. This information must be coupled with the absolute rate of photolysis of at least one species such as NO_2 to compute the appropriate photolysis rate constants.

Also important is the characterization of the initial contaminant loading in the chamber. When mechanisms overpredict the length of the induction period in which radical concentrations are initially building up, it may be due to the presence of an absorbing species either in the gas phase or on the walls that photolyzes. Actual measurement of the species accounting for these effects is complicated by their low concentrations.

When these effects are not adequately characterized one usually begins by parameterizing the NO_2 photolysis rate constant k_1, the initial concentration of trace photolyzable species such as HONO, and the wall

absorption rate of ozone. If still less is known about the experimental situation, the value of simulating the data becomes questionable.

The third major set of unknowns in simulating laboratory systems concerns the reactions which take place heterogeneously, either on the walls or on aerosols. Many reactions are thought to take place heterogeneously.

$$NO + NO_2 + H_2O \rightleftarrows 2HONO$$

$$NO_2 + NO_3 + H_2O \rightleftarrows 2HNO_3$$

which produce nitrous acid and nitric acid. Evidence for the heterogeneous nature of these processes comes from the strong dependence of measured rate constants on the reactor surface to volume ratio. (The disappearance of SO_2 in smog chamber experiments also seems to have a strong heterogeneous component either as a result of reactions in droplets or the wall-catalyzed formation of polymeric sulfur-oxygen species that remain on the walls as films.) Recent work has shown that certain long-lived free radicals such as HO_2 can be lost to particles at appreciable rates. Diffusion and subsequent loss of radicals to reactor walls occurs constantly but these processes do not affect the homogeneous chemistry appreciably. Heterogeneous processes, in general, are difficult to account for in kinetic mechanisms and are usually ignored.

In summary, the three classes of phenomena that often require parameterization in kinetic mechanisms are the homogeneous chemistry, the behavior of the chemical reactor, and heterogeneous chemistry. Tuning the model to account for unknown or uncertain chemical and physical effects is a legitimate procedure provided that the exact steps taken are spelled out in detail and lie within physically realistic bounds. A properly tuned mechanism is capable of predicting the concentration-time profiles of the stable species such as NO, NO_2, O_3, and hydrocarbons

within 10-20% over a wide range of initial conditions. In theory, such a mechanism, minus the steps included to account exclusively for chamber effects, should be capable of predicting atmospheric concentrations with the same accuracy.

REVIEW AND ANALYSIS

Kent R. Wilson

ABSTRACT

The question of the utility for urban oxidant control strategies of present Physical-Chemical Models (PCMs) for oxidant air quality is addressed. Alternative models for calculating oxidant levels from precursor levels are discussed: linear rollback, modified rollback, statistical models, smog chamber analogies, and PCMs. Sources of error in PCMs are described, including chemical reaction errors (initial conditions, sources and sinks, kinetic schemes, and computational limitations), errors in physical motion (windfields, omission of small scale motions, and grid size effects), and finally errors due to the approximate treatment of the interaction between physical motion and chemical reactions (turbulent inhomogeneity and its effect with nonlinear kinetics). The utility of present PCMs is categorized by particular usage: essential for scientific understanding, probably useful for comparison among different land-use, transportation, and both short and long term emissions control alternatives (but not for prediction of absolute levels), marginally useful for monitoring siting decisions, and unwise for use as legal standards. Several areas for improvement of PCMs are suggested, including (a) more general testing than just against monitoring data, (b) the theoretical and experimental investigation of the effects of turbulent inhomogeneity, (c) statistical extensions of PCMs to oxidant distributions, reduced kinetic schemes and model output statistics, (d) the use of specialized processors for greatly speeding up program execution and (e) the use of dynamic computer graphics to extract more understanding from the model calculations. It is concluded that while no model is as yet very accurate, an iterative approach is likely to lead to improvement of both models and of oxidant air quality.

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INTRODUCTION

The question that has been posed by EPA for this study is, "At the present time, are there any air quality simulation models sufficiently validated/evaluated and appropriate in designing urban oxidant control strategies?"

In answering this question we will first consider briefly the various alternatives for relating emission levels to oxidant levels, including rollback, smog chamber analogies, statistical/empirical relationships, and what we will call Physical-Chemical Models (PCMs); in other words, largely deterministic models that attempt to simulate those processes of physical motion and chemical reaction in the atmosphere involved in photochemical air pollution. Second, we will discuss some of the sources of error in PCMs, including input data, modeling of physical motion, chemical reaction, interaction between physical motion and chemical reaction, as well as errors involving comparison of theoretical model output with experimental measurements, both smog chamber and atmospheric measurements. Third, we will define utility and differentiate among a number of different ways of using PCMs in urban oxidant control strategies, concluding that the utility of PCMs ranges from essential to pernicious depending upon the specific mode and purpose of usage. Lastly, we will suggest a number of directions for improvement of PCMs.

ALTERNATIVE EMISSIONS TO OXIDANT MODELS

Several alternatives (54) exist for predicting oxidant levels as a function of hydrocarbon and (often) NO_x emissions levels, including simple and modified rollback, the drawing of analogies between reactions in smog chambers and in the atmosphere, various relationships derived from statistical/empirical analyses of atmospheric data, as well as the use of physical-chemical models. We will begin by admitting that there are *no* means at present to *accurately* predict atmospheric ozone levels as a function of emissions levels. All of

the above alternative approaches have substantial limitations and will continue for the foreseeable future to be less accurate than is desirable.

Nonetheless, each of the above approaches can be useful in the proper context, and we will survey these approaches briefly in order to set the context for a deeper discussion of the utility of PCMs.

Linear Rollback

Linear rollback results from the rather arbitrary assumption that there is a direct proportionality between reactive hydrocarbon (RHC) emissions in a region and maximum 1-hour average oxidant levels, and that this oxidant level will be reduced proportionately to reactive hydrocarbon reduction (55,56). Such an approach suffers from many defects. First, linear rollback only relates oxidant levels to reactive hydrocarbon emissions, yet such levels clearly also depend on NO_x emissions. Second, the chemical kinetics that link reactive hydrocarbon concentrations to ozone concentrations are known both experimentally and theoretically to be nonlinear, making suspect the linear rollback assumption. Third, the use of maximal 1-hour oxidant is statistically unfortunate, a nonrobust measure of the oxidant distribution that is an unstable indicator of the real atmospheric situation.

Modified Rollback

Modified rollback replaces the assumed linear relationship between RHC emissions and maximal oxidant with a statistical relationship based on atmospheric data. The most common version is the EPA Appendix J formulation (57-59), which relates the upper limit of maximal 1-hour oxidant levels to 6-9 a.m. nonmethane hydrocarbon concentrations. The Appendix J model has several serious problems, among them being neglect of NO_x emissions altogether, of post 9 a.m. RHC emissions, of transport (6-9 a.m. emissions and afternoon maximal oxidant are liable to relate to two different air masses), the nonrobustness of an upper limit curve that depends only on a few extreme measurements, the agglomeration of data from several cities with differing emissions and meteorological patterns and the possibility that the pattern of the oxi-

dant and nonmethane hydrocarbon data may be due more to mutual correlation to meteorological variation than to what would happen to oxidant levels if RHC emissions themselves were varied, given that the system is not linear.

Aerometric Statistical Models

Several attempts have been made to model the relationship between emissions levels and oxidant levels by statistical analysis of aerometric data (54). Merz, Painter, and Ryason regressed oxidant onto early morning NO_x and total hydrocarbon levels (60). Kinosian and Paskin (61) regressed oxidant levels onto NO_x concentrations for various classes of total hydrocarbon levels. Trijonis examined the joint distribution of morning hydrocarbon and NO_x levels and related this to downwind oxidant levels (62). Trijonis et al. (63) and Martinez et al. (64) examined recent historical trends in monitored oxidant and precursors levels, the relation among these trends providing a possible basis for predicting future effects of emission control measures. Caporaletti et al. (65) regressed hours over the Federal oxidant standard onto RHC picked up by simplified windstreams over an air basin, thus producing a statistical model that transforms a spatially resolved RHC emissions inventory into a predicted, spatially resolved, statistical oxidant distribution.

Such aerometric statistical models have two major advantages. First, they are based on observed atmospheric data, so that one might hope to make successful predictions even when an understanding of the underlying mechanism is not complete. The statistical relationships thus discovered might then lead to later deterministic understanding of cause and effect. Second, compared to PCMs, they are relatively easy and inexpensive to develop and to use, and thus can be applied both widely and repeatedly, for example, to the evaluation of many different land-use alternatives.

Statistical models, on the other hand, have limitations that should be carefully considered. A key problem is that while statistical models are derived from data from the recent past, they are often called upon to predict future oxidant levels from RHC and NO_x levels falling far outside the range of

- time dependent, both in emissions and in meteorology,
- spatially varying, both in emissions and in meteorology, and
- nonlinear with respect to variation of input variables because of the nonlinearity of the kinetic equations.

One could write down *ab initio* expressions that represent in theory the processes of interest as accurately as one desires, for example, microscopically as an exercise in time-dependent quantum mechanics, or on a more macroscopic level, in terms of hydrodynamics and chemical kinetics, we could describe the processes as:

$$\left(\frac{\partial}{\partial t} + \mathbf{ir}\cdot\nabla\right)c_i = R_i(\{c_i\}, T) + S_i(\mathbf{ir}, t),\ i = 1,\ldots,N \qquad \text{(Eq. 1)}$$

in which at time t, ir is the velocity at position ir, $\{c_i\}$ is the set of concentrations of the N chemical species involved, R_i is the rate of production of species i by chemical reaction at temperature T, and S_i represents the sources and sinks of species i as a function of position and time. The difficulty is that any *ab initio* approach is calculationally quite unfeasible. Thus a series of approximations are made, aimed at achieving a balance among what can be calculated, what can be measured, and what can be estimated. Instead of calculating rate constants from quantum mechanics (a presently impossible task for all but the simplest reactions), they are measured in the laboratory. Instead of calculating the large scale time evolution of the atmosphere, meteorological measurements are used for information on winds, temperature, humidity, and solar radiation. Instead of trying to calculate the small scale motions of the atmosphere, approximations are usually made such as K theory, neglect of effect of turbulent motion on averaged reaction rates, etc. (3,66,67). Several of the sources of error introduced by these approximations will be discussed in the following section.

General Observations

Now that the various alternative approaches for emissions to oxidant models are listed, we can make two general observations. First, all of the

the data used in the derivation. Such extrapolation leads to uncertainties that are difficult to estimate (54).

Smog Chamber Analogies

Smog chambers have provided much of our understanding of photochemical air pollution. From the time evolution of ozone concentration in an irradiated chamber as a function of initial precursor concentrations, one can draw analogies to the expected time evolution of oxidant in the real atmosphere as a function of emissions levels. By modeling the chemical kinetics of the reacting system and adjusting the rates of reaction and initial concentrations to match the chamber observations, one can hope to correct for chamber effects such as wall reactions and to extend the validity of the analogy beyond the range of the chamber experimental data base (12, 22, 23). Strengths of this approach include: (a) that it is calibrated to actual measured chamber experimental data over a range of RHC and NO_x concentrations, and (b) that it could be extended, at least in principle, to cover a variety of precursors, for example, different RHC mixtures. Weaknesses include: (a) that the effects of physical motion of the atmosphere, including transport, diffusion, mixing of air parcels of different histories and compositions, and the interaction between turbulence and chemical reaction are neglected and may be quite important, and (b) that chamber effects, such as wall interactions, may not in reality be removed by kinetic modeling corrections, as the tuning of the kinetic scheme may not correspond to the real chemical mechanism.

Physical-Chemical Models

The final alternative, and the one to which this study is most directly addressed, is the use of physical-chemical models in an attempt to simulate the atmospheric processes of physical motion and chemical reaction.

The need for physical-chemical models seems obvious. The phenomena of photochemical air pollution are too complex to be intuitively fully comprehended. We are dealing with a system that is:

above approaches have serious flaws, but all of them also have utility in the proper situation. There is, as yet, no way to transform even a perfectly accurate emissions distribution as a function of space and time into a satisfactorily accurate spatial-temporal ozone distribution. The real question, thus, is: How useful is a particular type of model under a specific set of circumstances? Second, the distinction between statistical and deterministic models is only one of degree. Statistical models are guided by deterministic understanding of cause and effect. Primary consideration is given to RHC and NO_x emissions in statistical models because of deterministic knowledge. Statistical aspects are included, at least implicitly, in all deterministic PCMs. Rate constants carry a statistical uncertainty, wind fields are constructed from scattered measurements, a whole ensemble of detailed atmospheric motions are consistent with all the available meteorological data, and the model itself is usually tuned in one way or another to match smog chamber and atmospheric observations.

SOURCES OF ERROR

Comparisons among PCMs and sources of error in PCM have been reviewed several times recently (18,19,68). Basically we can divide error sources into three categories: (a) chemical, having to do with concentrations and rates of reaction, (b) physical, having to do with atmospheric motion, and (c) chemical-physical interaction, having to do with the influence of motion on reaction.

Chemical Reaction Errors

Errors in the chemical aspects of PCMs are of four types: initial conditions, sources (emissions) and sinks, kinetics, and computational.

Initial Conditions--

Incorrect concentrations at $t = 0$ lead to errors in initial conditions for integrating approximate forms of Equation 1. For example, questions that can

be posed as initial condition uncertainty and involve long range transport (69-72) and multiday carryover of reactants, intermediates and products, form much of the basis of the serious disagreements as to the mechanism of elevated rural ozone (73-76).

Sources and Sinks--

Lack of knowledge of correct species resolved spatial-temporal distributions of sources of emissions and sinks, i.e., $S_i(ir, t)$ in Equation 1, remains a problem.

Kinetics--

No existing kinetic scheme (2,7,10,11,74,77) takes into account more than a fraction of the species and reactions that must be involved in photochemical air pollution due to the great variety of reactive hydrocarbons. Thus, one of two approximations is ordinarily applied, (a) picking a single hydrocarbon, for example propylene (2), as a surrogate for all reactive hydrocarbons, or (b) lumping hydrocarbons together into one or more classes (7). The first choice slights the chemical diversity of actual atmospheric reactive hydrocarbons but remains more faithful to measurable rate constants. The second choice allows an approximate match to the hydrocarbon distribution, but at the cost of the use of rate constants that are removed from direct measurement and represent average values or values arrived at by tuning a kinetic calculation to match an average result.

As Demerjian, Kerr, and Calvert (11) have warned, there is a danger in fitting rate constants to match gross smog chamber or atmospheric data in that the tuning may not represent the real mechanism and so may not give correct results when applied to a different situation with a different set of data. They remind us that "computer fits of experimental data based on such inaccurate choices of kinetic data obviously provide no validation of the mechanism choice, but represent a sophisticated exercise in curve fitting."

Other areas of concern are (a) how to include heterogeneous reactions, both involving aerosols and surfaces that may act as sinks, (b) a general lack of certainty in our knowledge of rate constants as well as possibly more subtle effects, such as (c) the production of unrecognized electronically metastable or vibrationally excited product states that might react rapidly before being quenched (78).

Computational Limitations--

Other sources of uncertainty arise not from errors in the data input or the differential equations used but rather from the limits to affordable computation time that determine the fineness of the spatial and temporal mesh size that can be integrated. For example, a reactive point source may be simulated incorrectly if it is spread out over a sizable grid cell, particularly given the nonlinear nature of the kinetics (79). Comparisons of model output representing averages over a grid cell may be incommensurate with monitoring station readings that represent a microscale environment (66,67).

Physical Motion Errors

Errors in modeling the physical motion of the atmosphere can be divided into three categories: external factors, approximations in the formulation, and computational limitations.

External Factors--

Given that the usual approach is to define a wind field from rather sparse and largely ground-level observations, the possible errors are considerable, particularly in periods of stagnation.

Approximations in Formation--

For computational practicality, small scale atmospheric motions are not treated explicitly, but instead usually handled by K theory, defining a

horizontal K_H and vertical K_V eddy diffusivity, which attempt to represent the averaged effect of small scale motions. This introduces the practical uncertainty as to what values to assign to K_H and K_V as a function of position and time. K_H is perhaps not important compared to horizontal advection, but K_V can certainly have a large effect. As an illustration, in Lagrangian modeling by Environmental Research and Technology (80), the values of K_V used vary by one and one-half orders of magnitude as a function of height and time.

Computational Limitations--

Because, given affordable computer time, only relatively large spatial-temporal grids can be used, the concentrations $\{c_i\}$ actually dealt with in the computations are spatially and temporally averaged, eliminating the direct calculation of the effects of any but larger scale motion. Again, this leads to incommensurability of prediction with the micro-scale measurements made at actual monitoring sites (66).

Chemical-Physical Interaction Errors

A possibly important source of error is the effect of calculating as homogeneously mixed an atmosphere that may in reality, due to the details of small scale motion, be chemically quite heterogeneous (81,82). Because of the nonlinearity of the differential equations representing reaction rates as a function of concentration, the approximation of using spatially and temporally averaged concentrations may lead to quite erroneous results. There is experimental evidence, for example, from the LARPP project, that the value of the ratio of

$$[O_3]\ [NO]/[NO_2]$$

varies by up to an order of magnitude from that expected from the photostationary state one would expect from a well-mixed system (80). A deeper analysis of these data by Calvert (83) indicates that the problem is worse in the early morning, when pockets of NO-rich air from surface emissions may be alternating

with pockets of aged O_3-rich air from higher elevations. That the problem is not just a local one is indicated by power plant plume measurements indicating persistence of NO/NO_2 inhomogenieties for up to 90 km downstream (84) and airborne O_3 measurements indicating inhomogeneities persisting even out to sea (71).

The *ad hoc* biasing of one or more homogeneous concentrations (80) to try to deal with this problem is clearly an unsatisfactory solution, and more sophisticated theoretical treatments (66 and private communication from J.H. Seinfeld, 1977), as well as additional experimental measurements, seem imperative.

UTILITY AND AREAS OF APPLICATION

As (a) there is no way to predict ozone levels as a function of emissions levels with great accuracy in any atmospheric situation, (b) the various uses of such predictions imply quite varied needs and constraints, and (c) there is the considerable variety described above of alternatives to PCMs for such prediction, the question as to the utility of PCMs in designing urban control strategies must be answered with discrimination as to specific use. As will be seen below, it is the author's belief that the utility of PCMs ranges from essential for some uses to disastrous in other contexts.

First, let us define useful as being significantly better than what is being done at present. In this way we can hopefully keep moving in the direction of improvement without being caught in the trap of inaction because of the inevitable imperfection of our ability to predict. We should candidly admit that oxidant prediction of all types is subject to large uncertainty (85), that the field is yet very young, and that no part of it is free from difficulties. Statistical/empirical modeling is often called upon to venture forth onto statistically unfirm ground to predict what would happen as a result of control strategies that would change the emissions pattern upon which the statistical analysis is based. Smog chamber experiments are conducted on too small a physical scale, with (a) the absence of both the large and small scale physical motions that characterize the atmosphere and affect

final ozone levels through transport and mixing and turbulent nonmixing effects on reactions, and (b) the presence of different boundary conditions (wall effects instead of natural sources and sinks). PCMs are up against a highly multidimensional problem that is really too complex, with too many unknowns for the state of our chemical and meteorological understanding and of our computational capacity.

Yet acknowledging all these problems, we can still gain more by using models where appropriate than by not using them. Even rollback tells us the direction to proceed with basin-wide hydrocarbon control and gives at least a rough figure for the magnitude.

We will now consider different possible applications for PCMs (19) and evaluate their utility in each case. The conclusions are summarized in Figure 1.

Short Term Prediction

If one could predict in advance the occurrence of oxidant episodes (54), one could then try to reduce their levels by short term emissions control strategies, for example, control of traffic and shutting down of particular industries. In addition health warnings could be issued.

Episode Prediction--

In the short term time scale, oxidant level changes are mainly determined by meteorological changes and not by emissions changes. These meteorological changes are controlled mainly by physical processes on a scale large compared to an air basin, and thus air basin deterministic models of PCM scale are inappropriate vehicles for such prediction. Statistical models (54), perhaps linked to large scale deterministic weather prediction models, are a more appropriate tool.

Conclusion: PCMs are unlikely to be useful for episode prediction.

Episode Control--

On the other hand, PCMs could be useful tools for the evaluation of urban short term emissions control strategies, to test the oxidant effect of varying traffic patterns or industrial emissions in response to an episode predicted by other means. A start in such a direction has already been made (86) in terms of evaluating air pollution emergency plans, although the pessimistic conclusions are somewhat in disagreement with a statistical analysis of the response of the real atmosphere to weekend-weekday variations in emissions (74). A kinetic study by the Bell Labs group (87), with a simplified physical motion component, of the weekend-weekday effect again points the way toward the use of PCMs in evaluating urban short term control strategies.

Conclusion: PCMs are probably already useful for episode control strategy evaluation.

Long Term Prediction

Several classes of uses exist for PCMs in long term control strategies, whose utilities need to be separately evaluated.

Scientific Understanding--

Control strategies should be evaluated from the basis of a thorough scientific understanding of photochemical air pollution, in order that the effects of alternative control strategies may be understood before a decision among them is made. PCMs are an essential part of the process of moving toward such a thorough scientific understanding. First, a PCM should ideally be an embodiment of present physical and chemical understanding, cast in a mathematical and algorithmic form approximating this understanding as closely as one can, given the strictures of data availability and computational cost. Given the multidimensional nature of the problem, with a spatially and temporally varying set of inputs being nonlinearly transformed to a spatially and temporally varying ozone output, there seems to be no reasonable alternative to PCMs for embodying and dealing with scientific understanding of photochemial air pollution.

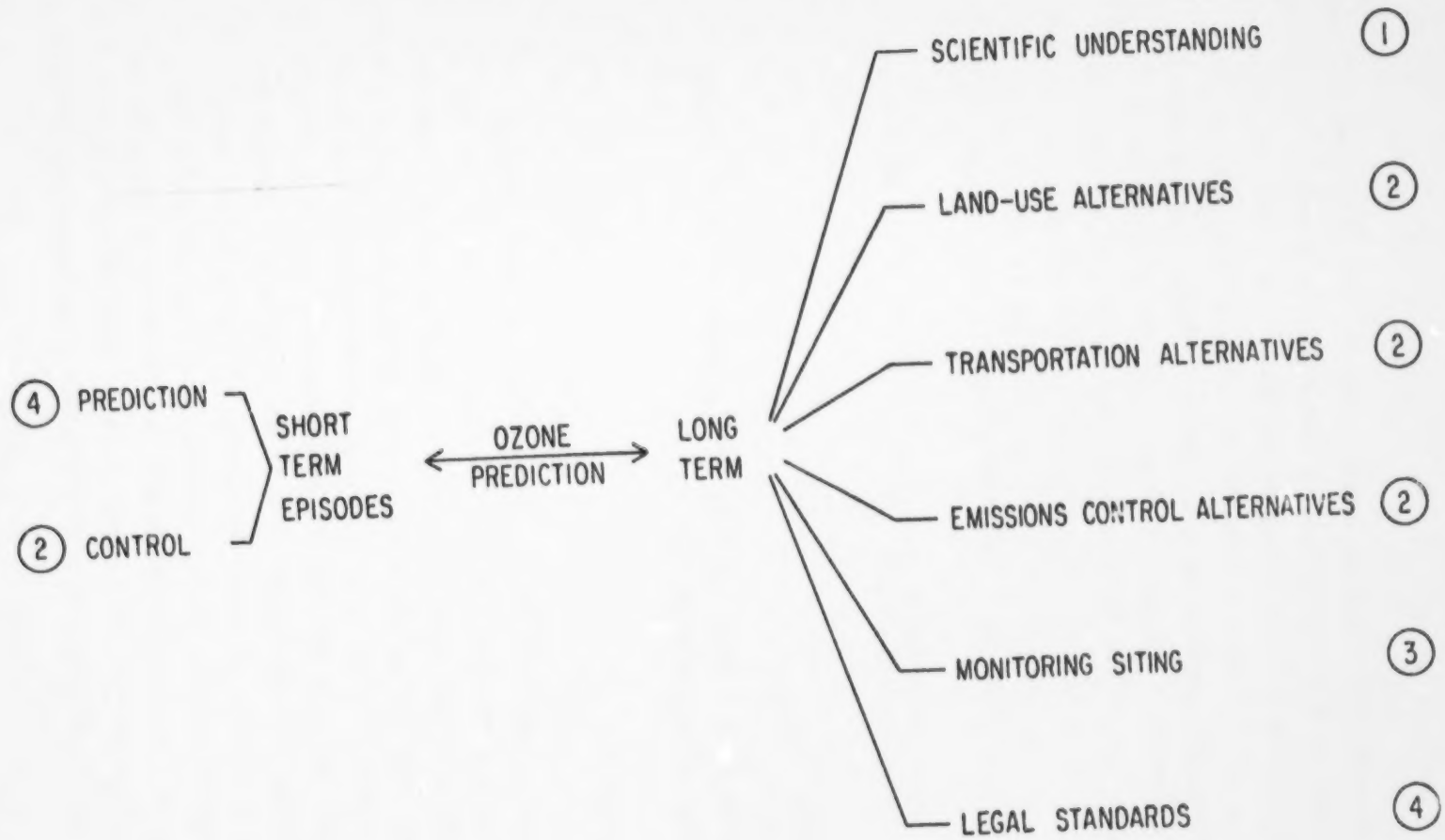

Figure 1. Uses and utilities of PCMs.
1 = essential, 2 = probably useful, 3 = possibly useful, 4 = probably the wrong tool.

In addition, because PCMs, in contrast with all other means of predicting ozone from emissions levels, are a simulation, an algorithmically parallel structure to scientific understanding, when the output of PCMs diverges from experimental evidence we must conclude that either: (a) the scientific understanding is incorrect or incomplete, (b) the approximations used in the solution are inappropriate, (c) an error in translating the scientific understanding into algorithmic form has been made, (d) there is insufficient data, or (e) the experimental evidence is incorrect. If the other error sources can be ruled out, then we can conclude that scientific understanding is indeed incorrect or incomplete. Thus PCMs can and must be used as a means to test scientific understanding against experimental data, and to prompt the improvement of this understanding when it is found wanting.

Conclusion: PCMs are essential to the improvement of scientific understanding of photochemical air pollution and thus to the rational choice among urban oxidant control strategies.

Land Use and Transportation Planning Alternatives--

Many emissions to oxidant approaches consider the air basin as a lumped unity. This simplifies the development and use of the prediction scheme, but is an inadequate approach for land use and transportation planning, which practically must consider geographical placement of alternative sites and the spatial distribution of their oxidant effects. An implicit assumption of lumped basin models is that the spatial distribution of emissions sources remains constant. By contrast, one of the needs of land use and transportation planning alternatives is the evaluation of the effects of changes in this distribution.

Thus spatial resolution in terms of emissions input is a key need for land use and transportation planning alternatives, and spatial resolution in oxidant output is useful in that it allows integration over population distributions and thus the calculation of relative dosage among planning alternatives. While statistical models with spatial resolution are possible and have been implemented (65,88), the use of PCMs is certainly a reasonable goal.

In this context, however, caution must be exercised. As is discussed below, the use of PCMs in the foreseeable future for the definition of legal standards for land use and transportation plans would probably be counter-productive. Thus, PCMs at this time would be most valuably employed as refinement tools, to best distribute emissions over a region to minimize population dosage (65), once total levels have been set by the application of other standards.

It should be realized that to do this, PCMs need to be evaluated for enough meteorological regimes that a weighted distribution of effects can be calculated that reasonably represents the meteorological distribution for the region.

In such a situation, where the aim is to choose among different spatial distributions of emissions, it is the author's opinion that existing PCMs could play a useful part.

Conclusion: Existing PCMs, if properly used, could play a useful role in choosing among urban land use and transportation alternatives providing different emissions pattern distributions, if the overall emissions totals were already set.

Emissions Control Alternatives--

Emissions control alternatives that involve differing controls on various classes of emitters entail not only differences in aggregated emissions totals for RHC and NO_x, but also (a) changes in the relative levels between RHC and NO_x emissions, (b) alternative distributions among various individual hydrocarbons, and (c) alternative spatial and temporal distribution patterns, for example, power plant NO emissions from elevated stacks versus ground-level rush hour peaked NO emissions from mobile sources. While it would be unwise to expect to predict absolute oxidant levels with accuracy, PCMs can be expected to provide relative guidance among such control alternatives (89). Again, weighting by meteorological regime distribution would seem important.

The question has been raised as to whether the Bell Labs model (2), in particular, is sufficiently validated to use in strategy evaluation. First, it should be noted that while the chemical kinetic scheme of this model is very extensive, the physical portion of the model is as yet rudimentary, involving only a few well-mixed boxes, into which emissions are immediately distributed with spatial resolution only on the scale of a county. Second, only one hydrocarbon, propylene, is used as a surrogate for all RHCs. In addition, trapped O_3 is treated in a rather arbitrary fashion. Thus, at this stage, the absolute agreement with monitoring station measurements must be regarded as likely to be somewhat fortuitous. One would hope to see this model evolve toward a better balance of attention to chemical reaction and atmospheric motion, and then to see an error analysis in which the sensitivity of the model to parameter change and the uncertainty in parameter values are jointly evaluated to establish error estimates. All of this is to say that one should not expect great absolute accuracy of any PCM, and in particular, not from an effort which, although very commendable and extensive for such an early stage, still has a maturing process of balancing and testing to go through.

Conclusion: PCMs could probably be used to provide relative guidance among emissions control alternatives, but should not be relied upon to provide absolute levels.

Monitoring Station Siting--

Monitoring stations should be sited so as to pick up the most information on pollution distributions for the least number of stations. PCMs could be used (again a distribution of meteorological regimes would be an improvement) to evaluate approximate oxidant distributions for use in decisions on monitoring station siting. In actual practice, it is likely to be more cost effective to use a combination of mobile stations for probing and then uncertainty reduction techniques for sampling that have been extensively developed for petroleum and mineral prospection.

Conclusion: PCMs are possibly useful for monitoring station siting, but unlikely to be cost effective unless they are already implemented for another purpose.

Legal Standards--

In the context of legal standards for oxidant control strategies, a major emphasis must be placed upon having a simple set of rules that can be interpreted by many users with minimal variability as to conclusions drawn. PCMs do not fulfill this need. Drawing legal standards in terms of PCMs would likely lead to confusion, extensive litigation, and a loss of momentum in the implementation of control strategies. Our legal system is not suited to probabilistic decision making and cannot be expected to deal easily or well with rules and regulations with multidimensional uncertainty.

The difficulty with using PCMs as legal standards is that there are too many parameters (reaction rates, initial conditions, eddy diffusion values, etc.) whose uncertainty is sufficiently great that by judicious (but not unreasonable) choice one could arrive at any point within a wide range of final absolute oxidant predictions. To attempt to settle such a situation in the context of litigation is an unpleasant prospect and should be avoided at the outset.

Conclusion: PCMs are inappropriate as legal standards because the multidimensional parameter uncertainties are too complex to handle in the context of litigation.

DIRECTIONS FOR IMPROVEMENT

Several areas are obvious ones for needed improvements in PCMs: better emissions inventories differentiated as to RHC type, measurement or improvement of particular rate constants, more three-dimensional windfield and temperature information, better determination of vertical eddy diffusivities, improved measurements of initial conditions, and better micromodeling to match individual monitoring test sites. In what is to follow, five aspects out of many possibilities for improvement are selected for discussion, (a) model testing, (b) the interaction between physical motion and chemical reaction (c) statistical improvement, (d) computer improvements and (e) improved interaction with the user.

Model Testing

Given the error sources cited above, in the simulation of chemical reactions (initial concentration conditions, sources and sinks of species, imperfections in the kinetic scheme, and computational limits to grid size), in the modeling of physical motion (lack of knowledge of gross wind field, approximations to avoid calculation of small scale motions, practical computational limits to resolution), and in the simulation of the interaction between small scale motion and chemical reaction due to turbulent inhomogeneity and nonlinear kinetics, one must certainly test such PCMs against experimental reality.

It is important to realize that it is not enough just to get the right final answer from the simulation; that it is not sufficient just to predict ozone levels reasonably for a given situation. If one is going to have confidence in using the model to predict the outcome in an altered set of circumstances (for example, the effect of a control strategy that would considerably alter emissions), the underlying chemical and physical mechanisms in the model must be correct and not just tuned in a multidimensional curve - fitting procedure to give the right numbers in a particular case.

Thus it is important to test the individual components of the model against experimental reality to insure their faithfulness to the actual chemical and physical mechanisms and not just to test the model as a whole.

For example, as is common, the kinetic schemes used in PCMs should be carefully checked against both measurements of individual rate constants and against smog chamber measurements. We should not be satisfied in the long run with the practice of sweeping the unknowns under the rug by tuning concentrations and rates to make the kinetic schemes agree with particular smog chamber results. The goal should be to understand both the experimental and the modeling situation thoroughly enough that we can quantify the true mechanism. Then, on the basis of such understanding, one can find appropriate approximations to speed up the computation, approximations whose validity can be checked against the true mechanism.

Similarly, the physical motion aspects of the model should be checked independently of the chemistry. Wind fields constructed with partial data can be checked against the rest of the wind measurements. Vertical wind and temperature calculations can be checked against further elevated measurements. Transport calculations can be checked against tracer studies, both specific release and CO distributions. Eddy diffusivity calculations can be checked by tracer studies, perhaps by smoke release.

The interaction of physical motion and chemical reaction is of particular concern, and is treated next.

Interaction Between Physical Motion and Chemical Reaction

As is discussed above, there is both theoretical and experimental evidence that the atmosphere is not well mixed and that this could lead to significant errors in PCMs. It would seem that a high priority should be placed on both theoretical (66) and experimental studies of this problem, as there are grounds for believing that both may be fruitful. For example, two rapid response NO, NO_2, and O_3 monitoring systems could be set up and their cross-correlations measured as a function of distance between inlets. In this way the spatial-temporal structure of concentration variations could be measured, and these measurements could be repeated under various conditions, such as near a freeway, far downwind from sources, at elevated locations, etc.

The question of "non-mixedness" needs to be resolved, as it gives rise to uncertainty both as to the accuracy of present PCMs and as to the applicability of smog chamber measurements for atmospheric analogy.

Statistical Improvements

It would seem worthwhile to investigate the incorporation of three statistical aspects into the now largely deterministic PCMs, (a) an ensemble of meteorological regimes in an attempt to model not just worst days but the yearly distribution of ozone, (b) a statistically determined reduced kinetics

package for greater speed, and (c) a version of model output statistics for predicting ozone at specific monitoring stations.

Meteorological Regimes--

The idea has been suggested that one should not just model worst days, but enough different categories of days that one can transform an emissions pattern into a predicted yearly ozone distribution. Again, the transformation is a nonlinear one, so that the shape of the ozone distribution is not precisely preserved under scale changes of the emissions pattern. (Perhaps this project is already underway in the San Francisco Bay Area where Smalley patterns have already been defined for meteorological regimes.) Certainly a system that predicted an ozone distribution, or at least the number of hours over the Federal standard, would provide easier comparison with mandated air quality goals (65,81).

Reduced Kinetics--

If a PCM is to be applied repetitively, for example, to evaluating land use and transportation alternatives, a large fraction of the computer expense might be saved by statistically developing a reduced chemical kinetics module (Private communication from W.S. Meisel, Technology Service Corp., 1974) (81). For such a use, one needs a black-box with only a few input-outputs (perhaps a few categories of RHC concentrations, NO, NO_2, O_3, and sunlight intensity). One does need, however, to have confidence that over the range of variables of interest, the reduced scheme does give the same answer as a more complete scheme. This is a statistical task, both to sample the range of the variables of interest and then to fit a simpler model to the calculated points. In other words, the suggestion is to work downward, systematically reducing a larger kinetic scheme in which one has confidence, rather than starting with a simplified scheme and trying to tune it to match particular measurements.

Model Output Statistics--

An alternative to the buildup of microscale models (66) to bridge the gap between PCM grid-cell scale output and the specific environment of a particular monitoring station would be the adoption of the Model Output Statistics (MOS) viewpoint from weather forecasting (76). One would then regress the oxidant readings at a particular station back onto several variables, involved in and predicted by the PCM, to arrive at a statistical scheme relating PCM output and specific monitoring station oxidant level. Such a scheme would be useful in evaluating situations in which emissions do not grossly change, but should be used with caution in cases in which emissions are greatly changed from those used to develop the MOS.

Faster Computers

Some guidance can perhaps be found in considering the development of other modeling fields in which computation involving the solution of large sets of coupled differential equations is also involved, fields such as stellar, plasma, and molecular dynamics. Two key developments are the move toward specialized processors to speed up the computation and dynamic computer graphics to allow the user to better extract understanding from the calculation.

PCMs fit the criteria for advantageous use of specialized processors. First, they involve in their exercise the repetitive use of the same or similar code, so that run costs, if they were really used widely, would be large compared to coding costs, which are higher for specialized processers. Second, they are amenable to being split into parallel streams, which need communicate only when a step is completed, and thus parallel hardware can be employed.

The present limits of computer expense by such techniques could be pushed back by two or three orders of magnitude. For example, a specialized system that runs approximately one-fourth as fast as a CDC 7600 for molecular dyna-

mics is now running (90), and the processor cost for this machine, which is available 24 hours per day, is approximately $65,000. On a larger scale, a machine for solving aerodynamic-coupled differential equations is being proposed by NASA (91), which will run 100 times faster than a CDC 7600 and whose price is estimated at $30 million. Perhaps somewhere in between there is a cost effective solution for PCMs.

Computer Visualization--

In other related modeling areas (90), dynamic computer graphics has proved very useful in allowing the user to comprehend the multidimensional time evolution of complex systems. Thus one could watch the time evolution of various species' concentrations as well as the wind field, all perceived three-dimensionally, and thus visualize what is rather incomprehensible when presented as tables of numbers.

CONCLUSIONS

None of the several alternative routes to predict oxidant levels from precursor emissions, linear rollback, modified rollback, aerometric statistical models, smog chamber analogies, or Physical-Chemical Models (PCMs) are capable of the accuracy desirable for evaluating urban oxidant control strategies. Yet each is useful in the proper context. Rollback is arbitrary; Appendix J is statistically unsound; statistical models are on shaky ground outside the range of the data used to develop them; smog chamber analogies leave out the effects of transport, mixing, and turbulent inhomogeneity and, in addition, involve surface effects different from the real atmosphere; and PCMs require large data inputs, large amounts of computer time, and involve approximations in chemical kinetics and small scale motions that lead to error.

Thus the utility of PCMs, like other models, needs to be evaluated in the context of particular usage. The view presented in this paper is that existing PCMs are essential for the scientific understanding of photochemical air pollution, and that they are probably useful for the choice among urban land use and transportation alternatives and for choosing among emissions control alternatives both for the short and long term as long as they are not used to set absolute goals. PCMs appear only marginally useful for monitoring station siting, and their use is judged to be most unwise as legal standards.

In conclusion, a feedback approach (63,92) to urban oxidant control is endorsed, with the realization that oxidant control probably will still be an issue 25 years from now. Control should be looked at as an iterative process in which we make the best judgment we can at each stage, realizing our fallibility, but as progress is made we continue to re-evaluate the system. We cannot expect perfection from PCMs now or in the future, but we can look for improvements both in the atmosphere and in our ability to model it.

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